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THE RAMAN SPECTRA OF ARAGONITE, STRONTIANITE AND WITHERITE

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(*Memoir No.* 121 *from the Raman Research Institute, Bangalore*-6)

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1. Introduction

In view of their isomorphism a comparative study of the Raman spectra of aragonite, strontianite and witherite is of interest. The vibration spectrum of the aragonite structure was discussed theoretically by Bhagavantam and Venkatarayudu (1939) and also by Couture (1947). Amongst the earlier experimental investigations on this subject the most complete are those of Couture (1947) and of R. S. Krishnan (1950) on aragonite, of T. S. Krishnan (1956) on strontianite and of Narayanan and Lakshmanan (1958) on witherite. Nevertheless, it was thought desirable to reinvestigate the subject and the present study has in fact revealed some new features of interest and shown the necessity for a reinterpretation of some of the observed facts. The present study has also enabled the various features observed in the three cases to be correlated with the differences in detail of the crystal structures. We shall in the following first briefly summarize the results of the theoretical analysis and discuss thereafter the experimental facts.

2. The Dynamics of the Aragonite Lattice

The three substances crystallize in the holohedral class of the orthorhombic system and belong to the space-group D_{2h}^{16} and contain four molecules per unit cell. The following salient features of the structure are of interest and help in our discussion of the observed facts. The structure of these crystals can be imagined as a distorted version of a hexagonal close-packed lattice of cations by compression along the y and z axes, the carbonate group lying at the centre of the hexagonal cell and between six cations (Bragg, 1924). The structure perpendicular to the z-axis consists of a series of planes of the cations which form the hexagonal network and sandwiched between every pair of these planes are two planes of the CO_3 groups which lie almost parallel to the xy plane. The CO_3 groups on either side of any cation plane are stacked one above the other and are in a staggered configuration with respect to each other owing to the centre of inversion lying midway between

them. The structure thus differs from the case of calcite wherein there is only one CO_3 plane situated midway between two Ca planes. Besides, whereas in the calcite structure each oxygen of the CO_3 group is in contact with two cations, in the aragonite structure each oxygen is in contact with three cations. It should also be mentioned that the cations, and carbon atoms and one oxygen atom of each CO_3 group are situated on the plane of symmetry σ (yz), the two other oxygens of each CO_3 group lying symmetrically on either side of this plane.

In Table I below are shown for the three crystals the lattice constants, refractive indices for vibrations parallel to x and y axes and the shortest distance between the cations and oxygens and the sum of the cation and oxygen ionic radii. In the case of an ideal hexagonal close-packing the ratio of the lattice constants a and b should equal $1:\sqrt{3}$. Columns 5 and 6 of Table I show the calculated values of b assuming the values observed for a and the differences between b and $\sqrt{3}a$. The distances are expressed in angstrom units.

TABLE I

Substance	c	a	b	$\sqrt{3}a$	$\sqrt{3}a-b$	n_z	n_y	Minimum R–O distance	R–O ionic radii
Aragonite ..	5·72	4·94	7·94	8·56	0·62	1·681	1·686	2·39	2·38
Strontianite ..	6·08	5·12	8·40	8·87	0·47	1·664	1·666	..	2·59
Witherite ..	6·54	5·25	8·83	9·09	0·26	1·676	1·677	2·76	2·75

The data shown in Table I clearly indicate that as we pass from aragonite to witherite the structure nearly approaches that of hexagonal symmetry. It is also seen that the interionic distances increase notably; hence, the coupling forces between the cations and the carbonate groups should diminish as we pass from the case of aragonite to witherite.

The group characters, selection rules and the number of vibrations under the different species are shown in Table II. The analysis reveals that, of the total number of 57 vibrations, 30 are active in Raman effect only, 21 are active in infra-red absorption only and the rest are inactive in both. The thirty Raman-active frequencies are separable into (i) external oscillations of the translatory and rotatory types of which there are 18 in all, and (ii) internal vibrations of the CO_3 groups of which there are 12 in all. As seen from Table II, oscillations of both translatory and rotatory types occur under each of the several representations and hence it is not possible

TABLE II

D_{2h}^{16}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	T	T′	R′	n_4'	R.E.	I.R.
A_{1g} ..	1	1	1	1	1	1	1	1	0	4	1	4	*p*	*f*
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	0	2	2	2	*p*	*f*
B_{2g} ..	1	−1	1	−1	1	−1	1	−1	0	2	2	2	*p*	*f*
B_{3g} ..	1	−1	−1	1	1	−1	−1	1	0	4	1	4	*p*	*f*
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	0	2	2	2	*f*	*f*
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	1	3	1	4	*f*	*p*
B_{2u} ..	1	−1	1	−1	−1	1	−1	1	1	3	1	4	*f*	*p*
B_{3u} ..	1	−1	−1	1	−1	1	1	−1	1	1	2	2	*f*	*p*

T = Pure Translations; T′ = Translatory oscillations; R′ = Rotational oscillations; n_4' = internal vibrations; R.E. = Raman effect; I.R. = Infra-red; *p* = permitted; *f* = forbidden.

to identify any observed frequency as arising from solely a rotational or translational oscillation. A detailed description of the numerous symmetry modes can however be found in the paper by Couture (1947). The large number of eighteen lattice frequencies permitted to appear in the Raman effect in the case of the aragonite structure is in striking contrast with the case of calcite wherein only two lattice frequencies of the doubly degenerate class are allowed; this difference evidently arises from the lower symmetry of the aragonite structure and also due to the presence of the increased number of groups in the unit cell of the structure.

Finally, we may remark that the 12 frequencies of the internal type arise owing to the coupling between the four CO_3 groups and due to the removal of degeneracy in the crystalline state and are correlated to the four frequencies of the free-ion as follows:—

ν_1 (Totally symmetric, A_1', 1063 cm.$^{-1}$) $\rightarrow A_{1g}$, B_{3g}

ν_2 (Out of plane mode, A_2'', 879 cm.$^{-1}$) $\rightarrow A_{1g}$, B_{3g}

ν_3 (Doubly degenerate, E′, 680 cm.$^{-1}$) $\rightarrow A_{1g}$, B_{1g}, B_{2g}, B_{3g}

ν_4 (Doubly degenerate, E′, 1415 cm.$^{-1}$) $\rightarrow A_{1g}$, B_{1g}, B_{2g}, B_{2g}.

Since the CO_3 groups in the case of aragonite and the other two crystals are not known to be distorted or different from the CO_3 groups in calcite, the removal of degeneracy in the cases of ν_3 and ν_4 and the Raman activity of vibrations corresponding to the Raman inactive vibration ν_2 of the free-ion have necessarily to be associated with the fact that the environment of

the CO_3 groups which are coupled to the cations lacks the trigonal symmetry. Hence, it follows that in the three crystals the splitting arising from the removal of degeneracy and the Raman activity of vibrations corresponding to ν_2 can be correlated with the fact of these structures departing from the perfect hexagonal structure to different extents as pointed out earlier.

3. EXPERIMENTAL DATA

The Raman spectra of the three crystals were recorded using the λ 2536·5 resonance radiation of the mercury arc for excitation. The details of the experimental techniques have already been described in an earlier paper by the author (1957). A medium quartz spectrograph was used to obtain intense records of the spectra. A Littrow quartz spectrograph of greater resolving power was also employed to reveal the fine structure of the lines. The crystals used were fairly small being $15\times10\times5$ mm. in size and were not altogether flawless and hence the length of useful exposure that could be given to record the spectra was limited. Exposures of the order of two days were given to record the spectra intensely. In the cases of strontianite and witherite—which were in the form of coarse lumps—the spectra recorded were for random orientations. In the case of aragonite the exciting radiation was incident on a prism face and the scattering was observed along the z-axis of the crystal. The spectrum of cerussite—which also has an isomorphous structure—could not be recorded since the specimens were opaque to the λ 2536·5 radiation. Its spectrum has however been reported and discussed in detail by Couture (1947), who used the visible radiations of the mercury arc for exciting the Raman effect.

In Plate V accompanying this paper are reproduced the spectra of the three substances, recorded with comparable intensity. The microphotometer records of the low-frequency region of the spectra recorded with the Littrow spectrograph appearing as Figs. 1, 2 and 3 in the text and those appearing in Plate VI clearly exhibit the numerous frequency shifts. Of these, 11 frequency shifts, *viz.*, 133 and 1037 cm.$^{-1}$ in aragonite, 135, 200, 711, 855 and 2142 cm.$^{-1}$ in strontianite, and 194, 237, 852 and 2116 cm.$^{-1}$ in the case of witherite have emerged from the present investigation.

The frequency shifts observed in the three cases are shown in Table III. Considerations of intensity and the general pattern of the observed shifts indicate that the frequency shifts shown against each other in the three cases arise in all probability from similar normal modes of vibration. The values of the frequency shifts reported herein are in fair agreement with those reported by the earlier investigators excepting in a few cases where the lines are diffuse and weak or exhibit fine structure. The frequency shift reported by Krishnan

(1950) at 1059 cm.$^{-1}$ in the case of aragonite is believed to be the intensely Raman active frequency of shift 1086 cm.$^{-1}$ excited by the mercury line λ 2534·8. It may be seen from Plate VI that this mercury line has similarly

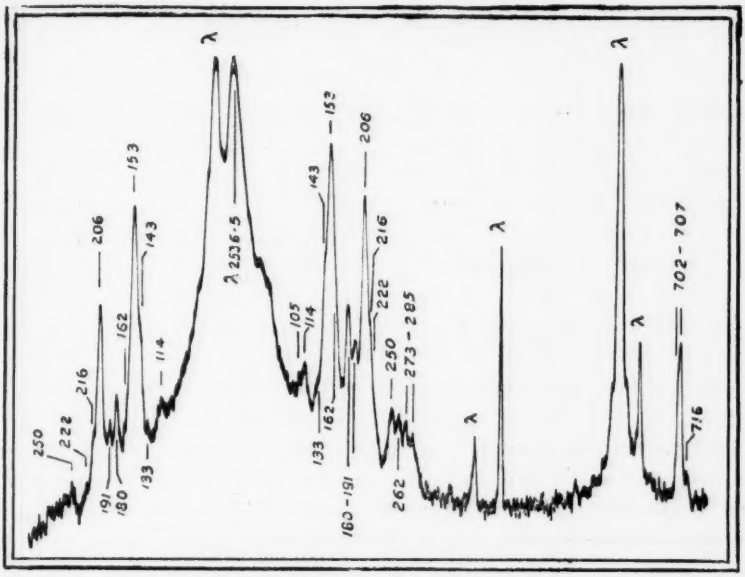


FIG. 1. Microphotometer record of the low frequency region of the Raman spectrum of aragonite.

excited the principal frequency shift in the cases of $SrCO_3$ and $BaCO_3$ as well. The frequency shift reported by him at 1574 cm.$^{-1}$ could not be confirmed owing to the presence at about this point of the diffuse mercury line λ 2642·48.

The following principal features are strikingly evident from the reproduced spectra and their microphotometer records. (i) Barring a few exceptions there appear in all the three cases similar patterns of frequency shifts of comparable intensity. (ii) Corresponding to the degenerate modes of the free-ion there appear in the three crystals a multiplicity of components. (iii) The frequency shifts themselves and the extent of separation between corresponding groups of lines diminish as we pass from the case of aragonite to witherite. (iv) The intensity of the frequency shift at about 860 cm.$^{-1}$ (corresponding to the Raman-inactive mode of the free-ion) diminishes as we pass from the case of aragonite to witherite. (v) The very low frequency shifts close to the exciting line show a notable increase in intensity as we

TABLE III

Observed Frequency Shifts in Cm.$^{-1}$

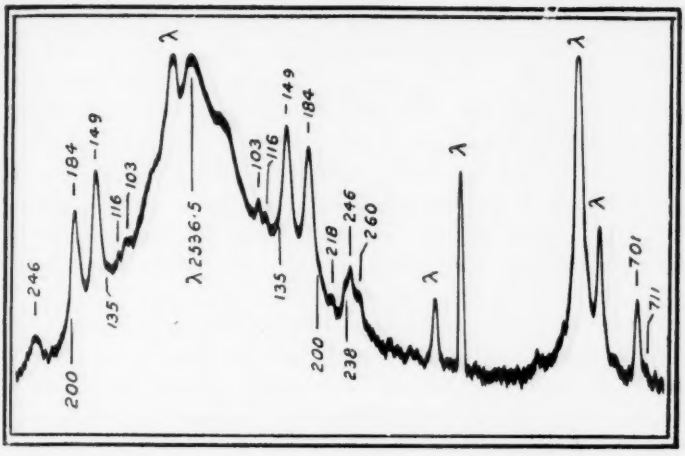
	Aragonite $CaCO_3$	Strontianite $SrCO_3$	Witherite $BaCO_3$
Lattice Oscillations ..	105 w. 114 m. 133 v.w.* 143 m. .... 153 v.s. 162 m. 180 s. 191 s. 206 v.s. 216 m. 222 v.w. 250 m. ..... 262 m. 273 m. 285 m.	.... 103 s. .... 116 s. ... 135 w.* 149 v.s. .... 184 v.s. .... 200 w.* 218 m. ..... 238 m. 246 s. 260 m.	76 m. 80 s. .... 90 s. 101 w. ..... 136 v.s. .... 153 v.s. 161 m. .... 178 m. 194 w.* 217 m. 227 s. 237 w.*
ν_3 ..	702 m. 707 m. 716 w.	701 m. 711 w.*	691 m. 699 w. ....
ν_2 ..	854 m.	855 w.*	852 v.w.* .....
ν_1 ..	1086 v.s.	1074 v.s.	1061 v.s. ....
ν_4 ..	1415 m. †1464 } 1463 s. †1466 }	1408 m. 1438 s. 1447 m.	1394 m. 1409 m. 1421 s. .....
$2\nu_1$ ..	2165 w.	2142 w.*	2116 w.*
Combinational shifts ..	1037 w.*(854+ 180) 1815 w. (743+1078)	....	1510 m.(1421+90)

Note.—The frequencies marked with an asterisk are reported for the first time. 1078 and 743 appearing in the last line of the table have been observed in the infra-red (*vide* Refs. 7 and 10).

† Resolved by Couture from polarisation studies.

s = strong; v.s. = very strong; *w* = weak; *m* = moderate intensity.

pass from aragonite to witherite. (vi) In each of the three cases a well-defined frequency shift appears which is clearly the overtone of the principal frequency shift.


λ
λ
λ

4. DISCUSSION OF THE RESULTS

The appearance in the spectrum of aragonite of 16 out of the 18 frequency shifts theoretically predicted is by itself proof of the strong coupling between the four molecules in the unit cell. Moreover, the observation in aragonite of three components in each of the cases corresponding to the degenerate modes ν_3 and ν_4 furnish further evidence of the coupling between the CO_3 groups. The earlier explanations of the frequency shifts observed at 1415 and 716 cm.$^{-1}$ in the case of aragonite as respectively the overtone of the frequency at 707 cm.$^{-1}$ and as a combination of the differential type, *viz.*, ($\nu_2 - 153$), are clearly untenable. Also, it may be remarked that (i) in the analogous and experimentally more favourable case of calcite the overtone of the line corresponding to ν_3 could not be observed at all and (ii) combinations of the differential type are usually too weakly Raman-active to be readily observed. The appearance of three lines corresponding to ν_4 and two lines corresponding to ν_3 in $SrCO_3$ and $BaCO_3$ also is in accordance with the splitting of ν_3 and ν_4 predicted by theory though the number of components observed is less than the predicted number.

The origin of the diminution of the internal frequency shifts and also of the diminution in the extent of splitting of the degenerate frequencies is to be sought for in the fact, that in the three cases the cations surrounding the CO_3 group are at increasingly greater distances as we pass from aragonite to witherite. Indeed, the diminution of the coupling forces are most strikingly exhibited by the shift of the principal Raman lines from a value of 1086 cm.$^{-1}$ in the case of aragonite to a value of 1074 cm.$^{-1}$ in strontianite and to 1061 cm.$^{-1}$ in witherite. As already indicated in Section 2 of this paper, the splitting arising from the removal of degeneracy would diminish as the structures approach that of perfect hexagonal symmetry. This, taken in conjunction with the fact of the increasing interionic distances and correspondingly reduced coupling between the groups, explains the fact of the diminution in the extent of splitting.

We may also remark upon the fact that whereas the frequency at about 860 cm.$^{-1}$ is observed with moderate intensity in aragonite, its intensity considerably diminishes as we pass on to the case of witherite. The frequency corresponding to the Raman inactive mode of the free-ion is actually observed in the crystalline state owing to the environment of the CO_3 group lacking the trigonal symmetry. As already mentioned the structure approaches that of hexagonal symmetry as we pass on to the case of witherite; the diminution in the intensity of this line is hence not surprising.

Polarisation studies enabled Couture to assign the two very intense Raman lines at 153 and 206 cm.$^{-1}$ in the case of aragonite to the species B_{2g} and B_{3g} respectively. The pair of intense lines observed in each of the cases of $SrCO_3$ and $BaCO_3$ also presumably belong to the species B_{2g} and B_{3g}. The analysis of the symmetry modes shows that the rotatory oscillations of the CO_3 groups about y and x axes involving large changes in polarisability fall under the classes of B_{2g} and B_{3g} respectively. The appearance of a pair of intense lines of the same species indicates that they might arise from predominantly similar movements, though coupling between them and other modes of the same species cannot be altogether excluded. The diminution in the values of these frequencies and the extent of their separation is consistent with the fact of the decreasing coupling forces and that of the structure approaching one of hexagonal symmetry as we pass on to the case of witherite.

The low-frequency lines close to the exciting line in the three cases may be attributed to mass movements of the CO_3 groups and the cations surrounding them as a whole; the pronounced diminution in the values of these frequencies because of the increase in the mass of the oscillating groups, and the gain in their intensity because of the greater refractivity of the cations as we pass from aragonite to witherite are all features consistent with each other. The lattice frequencies observed higher up in the region 220–250 cm.$^{-1}$ also diminish as we pass from the case of aragonite to witherite.

In the present study the spectra have been recorded with great intensity so as to reveal even faint lines. In spite of this it is seen from Table III that the total number of lines observed in each case is less than the number predicted by theory. The explanation that can be offered for this is that, either the frequency shifts overlap and are not resolved from each other, or that they are too weakly Raman-active to be recorded.

Finally, a few remarks may be made regarding the second order frequencies observed. There exists a small but systematic difference of the order of 4 cm.$^{-1}$ between the values of the fundamentals derived from the overtones and those of the observed Raman-active fundamentals. A simple explanation of this feature is that the observed overtone represents the combined effects of the four components theoretically permitted, *viz.*, A_{1g}, B_{3g}, B_{1u} and B_{2u} corresponding to the totally symmetric mode of the free-ion. The infra-red-active frequencies corresponding to this mode reported by Louisfert (1951) are respectively 1078 cm.$^{-1}$ in aragonite, 1072 cm.$^{-1}$ in strontianite and 1060 cm.$^{-1}$ in witherite indicating that they are indeed slightly lower than the corresponding Raman-active fundamentals. The explanations given in Table III for the combinational modes are only tentative and the

origin of their observable Raman-activity is not clear. However, it should be mentioned that the appearance of discrete well-defined frequency shifts in the second order spectrum is in consonance with the theory of lattice dynamics put forward by Sir C. V. Raman in 1943, and which predicts that the second order spectrum should exhibit the discrete character of the vibration spectra of crystals.

5. CONCLUDING REMARKS

As the crystals under discussion belong to the centro-symmetric class no exact coincidences can be expected between the data from studies on infra-red absorption and the Raman effect. The infra-red absorption spectra of these substances have been investigated by Louisfert (1951) and Narayanan and Lakshmanan (1958) and they report analogous features with regard to the splitting arising from the removal of degeneracy and the presence of a multiplicity of groups in the unit cell of the structure. However, the infra-red data for these substances are incomplete for the 7μ region of the spectrum. The striking multiplicity of frequencies observed in the Raman effect in this frequency region indicates the existence of similar effects in the infra-red also at 7μ.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

6. SUMMARY

The Raman spectra of the three crystals are recorded using the λ 2536·5 radiation of mercury and eleven new lines of low intensity are reported. These include the appearance in the cases of $SrCO_3$ and $BaCO_3$ of the line corresponding to the Raman-inactive mode of the free-ion, this line being of progressively diminishing intensity in the three cases owing to the structures progressively approaching that of hexagonal symmetry. The similarities and the differences observed in the three spectra are also correlated with the details of the crystal structures.

7. REFERENCES

1. Bhagavantam, S. and Venkatarayudu, T. .. *Proc. Ind. Acad. Sci.*, 1939, **9 A**, 224.
2. Bragg, W. L. .. *Proc. Roy. Soc.*, 1924, **105 A**, 16; see also *Strukturbericht*, Vol. 1, pp. 295 and Vol. 3, pp. 85.
3. Couture, L. .. *Annales de Physique*, 1947, **2**, 1.
4. Krishnamurti, D. .. *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 183.

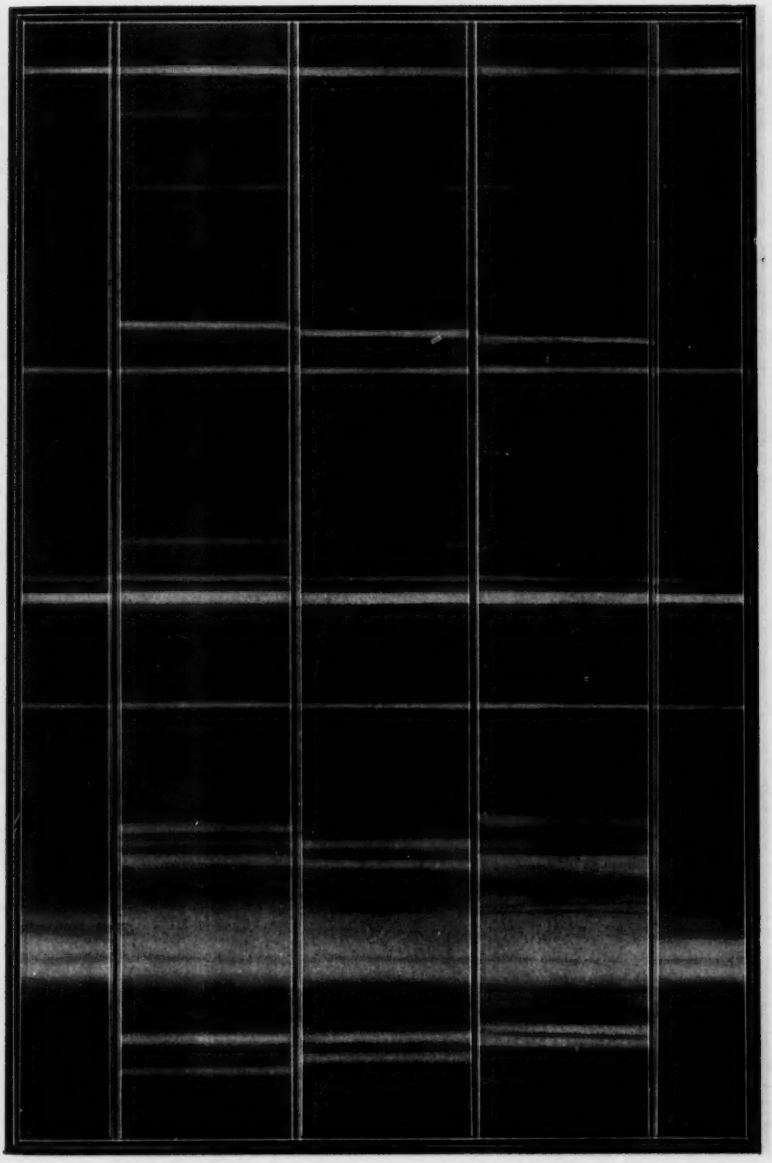


FIG. 1. The Raman spectra of the three crystals. (*b*). Aragonite; (*c*). Strontianite. (*d*). Witherite. (*a*) and (*e*). Spectrum of the mercury arc.

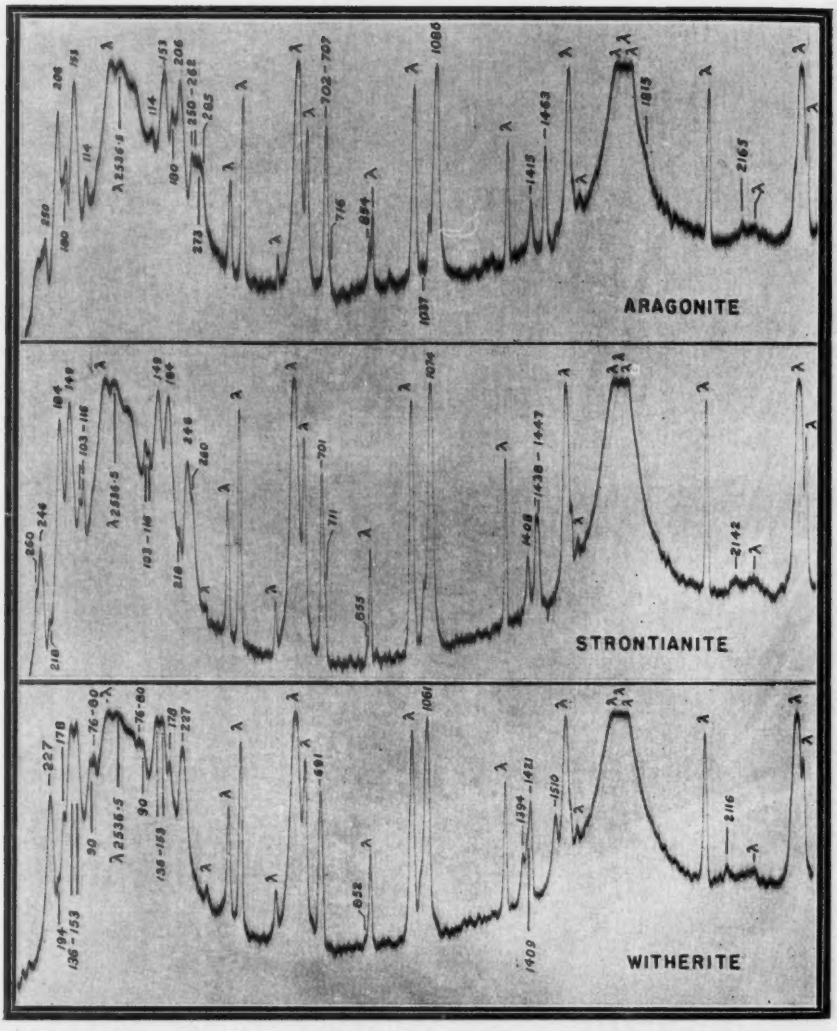


FIG. 2. Microphotometer records of the three spectra recorded with the medium quartz spectrograph.

5. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1950, **31 A**, 435.
6. Krishnan, T. S. .. *Ibid.*, 1956, **44 A**, 96.
7. Louisfert, J. .. *Compt. Rend.*, 1951, **233**, 381.
8. Narayanan, P. S. and Lakshmanan, B. R. *Jour. Ind. Inst. Sci.*, 1958, **40**, 1.
9. Raman, C. V. .. *Proc. Ind. Acad. Sci.*, 1943, **18 A**, 237.
10. Rawlins, F. I. G. and Rideal, E. K. *Proc. Roy. Soc.*, 1927, **116 A**, 140; see also *Landolt Bornstein Tables*, 1955, Vol. 1, Part IV pp. 605.
11. Roop Kishore .. *Proc. Ind. Acad. Sci.*, 1942, **16 A**, 36.

A NEW SYNTHESIS OF CATENARIN AND ERYTHROGLAUCIN

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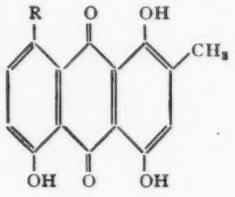
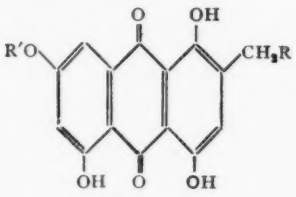
Among the naturally occurring polyhydroxy-2-methyl anthraquinones of fungal origin, islandicin (I), cynodontin (II), catenarin (III), erythroglaucin (IV) and tritisporin (V) possess a 1 : 4-dihydroxy system.



I, R=H
II, R=OH



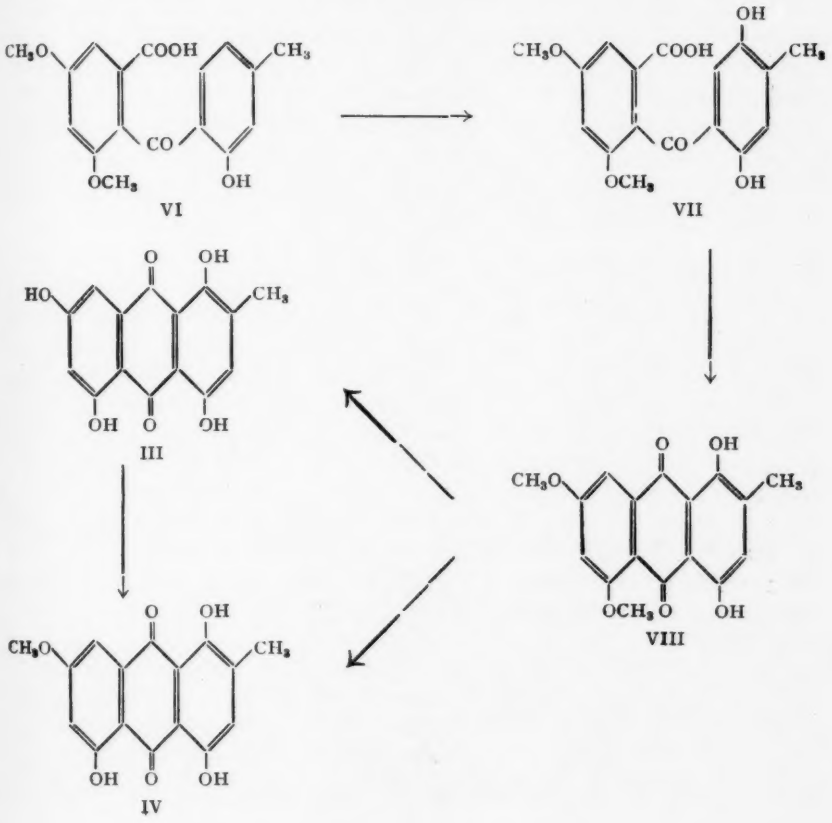
III, R=R′=H
IV, R=H; R′=CH_3
V, R=OH; R′=H

It has recently been suggested[1-2] that *para*-nuclear oxidation forms a stage in the evolution of these compounds and that this oxidation probably takes place in a preanthraquinone stage like the benzoyl benzoic acid stage. Following this suggestion a new synthesis of 2-methyl quinizarin, islandicin (I) and cynodontin (II) have recently been reported[3] using the *para*-nuclear oxidation procedure. This method has now been extended for the synthesis of catenarin (III) and erythroglaucin (IV) and is found to work very satisfactorily.

Catenarin (III) was first isolated[4] as a metabolic product of *Helminthosporium gramineum* Rabenhorst. Later, it was found[5] to be the main colouring matter of *Helminthosporium catenarium* Drechsler. Its constitution was established as (III) by Anslow and Raistrick[6] who also synthesised[7] it using a modification of the method used by Jacobson and Adams[8] for the synthesis of emodin. 3 : 5-Dimethoxy phthalic anhydride was condensed with *m*-cresol and the resulting benzoyl benzoic acid (VI) was brominated to give the bromoderivative. Ring closure was followed by demethylation and replacement of the bromine atom by hydroxyl. In the present synthesis

3:5-dimethoxy-2 (2′-hydroxy-4′-methyl)-benzoyl benzoic acid (VI) has been subjected to *para*-nuclear oxidation with alkaline potassium persulphate and the resulting quinol derivative (VII) cyclized using concentrated sulphuric acid and boric acid when a good yield of the dimethyl ether (VIII) of catenarin is obtained. It has been completely demethylated by boiling with a mixture of constant boiling hydrobromic acid and glacial acetic acid for 20 hours when catenarin (III) is produced. Partial demethylation using the same reagent and shorter time (2 hours) gives erythroglaucin (IV).

Anslow and Raistrick[6] established the structure of erythroglaucin as 7-O-methyl catenarin (IV) by partial methylation of catenarin (III) using methyl iodide and sodium methoxide and heating in a sealed tube. This partial methylation could be more conveniently carried out with good yields



using restricted amount of dimethyl sulphate (1 mole) and potassium carbonate in acetone medium.

EXPERIMENTAL

3 : 5-Dimethoxy-2-(2' : 5'-dihydroxy-4'-methyl)-benzoyl benzoic acid (VII)

3 : 5-Dimethoxy-2-(2'-hydroxy-4'-methyl)-benzoyl benzoic acid[7-8] (VI, 2 g.) was dissolved in a solution of potassium hydroxide (1·3 g. in 40 c.c. of water) and the solution cooled to 15–20°. A saturated solution of potassium persulphate (1·9 g.) in water was added with stirring in the course of two hours and the mixture was kept at room temperature overnight. The dark red reaction mixture was acidified to congo red and the separated unreacted benzoyl benzoic acid was filtered ; for removing last traces, the filtrate was extracted with ether twice. To the aqueous solution were added sodium sulphite (1 g.) and concentrated hydrochloric acid (16 c.c.) and the mixture heated on a water-bath for 20 minutes. On cooling a light brown solid separated which was filtered and washed with a little water. It crystallised from dilute ethanol as clusters of light brown prisms, m.p. 234–35° ; yield, 1·7 g. (Found: C, 61·4 ; H, 4·9 ; $C_{17}H_{16}O_7$ requires C, 61·4 ; H, 4·8%). It gave a green colour with alcoholic ferric chloride which turned brown on keeping. With aqueous sodium carbonate and sodium hydroxide it gave a yellow colour changing to red.

1 : 4-Dihydroxy-5 : 7-dimethoxy-2-methyl anthraquinone (VIII)

The nuclear oxidation product (VII, 1·5 g.) was heated with a mixture of melted and powdered boric acid (1·5 g.) and concentrated sulphuric acid (25 c.c.) on a water-bath. At 70°, fuming sulphuric acid (3·8 c.c.) was added and the mixture was allowed to stand for an hour at that temperature. The deep blue solution was then poured on crushed ice and stirred well. The precipitate was coagulated by heating on a steam-bath for 15 minutes. It was cooled, filtered and washed with hot water. The red solid crystallised from acetic acid as plates. It was further purified by sublimation in vacuum at 160·65° and finally crystallised from ethanol ; red needles, m.p. 212–13° ; yield, 1·2 g. (Found: C, 64·5; H, 4·6 ; OCH_3, 18·4; $C_{17}H_{14}O_6$ requires C, 65·0 ; H, 4·5 ; 2-OCH_3, 19·7%).

It was readily soluble in chlorofrom, moderately soluble in glacial acetic acid and less soluble in alcohol. It was insoluble in aqueous sodium bicarbonate and sodium carbonate, but soluble in aqueous sodium hydroxide and potassium hydroxide giving bluish violet solutions from which a violet precipitate separated on standing. With concentrated sulphuric acid it

gave a deep blue colour and with methanolic magnesium acetate a pink colour.

Catenarin tetramethyl ether.—The above dimethoxy compound (VIII, 0·2 g.) was methylated with dimethyl sulphate (1 g.) and anhydrous potassium carbonate (2 g.) in boiling acetone solution (6 hours). The product crystallised from acetone as golden yellow leaflets, m.p. 190–91°; yield, 0·15 g. (Found: C, 66·5 ; H, 5·7 ; $C_{19}H_{18}O_6$ requires C, 66·6 ; H, 5·3%).

Catenarin (1 : 4 : 5 : 7-*tetrahydroxy*-2-*methylanthraquinone, III*)

The above dimethyl ether (VIII, 0·5 g.) was refluxed with glacial acetic acid (50 c.c.) and hydrobromic acid (constant boiling, *d.* 1·8 ; 75 c.c.) for 20 hours. The product was filtered hot and the filtrate cooled in ice, when a red solid separated. It was filtered and stirred with 2% aqueous sodium carbonate (75 c.c.) in which it dissolved almost completely. The filtered solution was acidified and the precipitate was filtered and crystallised repeatedly from alcohol yielding red plates, m.p. 245–46° ; yield, 0·25 g. (Found: C, 62·5 ; H, 3·7 ; $C_{15}H_{10}O_6$ requires C, 62·9 ; H, 3·5%). It agreed in all its properties with an authentic sample of catenarin ; a mixed melting-point with the latter showed no depression. Its ultraviolet spectrum in ethanol had $\lambda_{max.}$ 230 (log ϵ 4·52), 256 (log ϵ 4·23), 280 (log ϵ 4·28), 303 (log ϵ 4·05) and 490 (log ϵ 4·17) agreeing with the natural sample. In the earlier record[9] 298 mμ was reported for the natural sample in place of 303 mμ. But the natural sample we have examined gives the absorption at 303 mμ.

The acetate was prepared by treating a solution of catenarin in acetic anhydride with a drop of concentrated sulphuric acid, allowing the solution to stand for an hour and pouring it on crushed ice. The product was crystallised from ethyl acetate yielding lemon yellow rods, m.p. 234–35°, agreeing with the earlier record.

Erythroglaucin (1 : 4 : 5-*trihydroxy*-7-*methoxy*-2-*methyl anthraquinone, IV*)

(*i*) *Partial Demethylation.*—1 : 4-Dihydroxy-5 : 7-dimethoxy-2-methyl anthraquinone (VIII) (0·3 g.) was treated with glacial acetic acid (30 c.c.) and hydrobromic acid (45 c.c.) and the mixture heated under reflux for two hours. The product was filtered and the filtrate cooled in ice. The solid which had separated, was filtered and crystallised from glacial acetic acid yielding deep red plates, m.p. 205–06° ; yield, 0·2 g. (Found: C, 63·5 ; H, 4·1 ; $C_{16}H_{12}O_6$ requires C, 64·0 ; H, 4·0%). It agreed in all its properties with an authentic specimen of erythroglaucin ; a mixed melting-point

with the latter showed no depression. Its ultraviolet spectrum in chloroform had $\lambda_{max.}$ 277 (log ϵ 4·28), 305 (log ϵ 4·06), 355 (log ϵ 3·26) and 495 (log ϵ 4·18) agreeing fully with the natural sample.

(*ii*) *Partial methylation of catenarin.*—Catenarin (0·1 g.) was dissolved in boiling acetone (10 c.c.) and dimethyl sulphate (0·035 g.) and anhydrous potassium carbonate (1 g.) were added and the mixture heated under reflux for 4 hours. The mineral salts were removed by filtration and thoroughly extracted with acetone. The solvent was evaporated and the residue stirred with 2% aqueous sodium carbonate and filtered. The red solid thus obtained crystallised from glacial acetic acid as deep red plates, m.p. 205–06° ; yield, 0·08 g. The melting-point was unaffected by mixing with an authentic sample of erythroglaucin.

SUMMARY

A convenient synthesis, following suggested path of biogenesis, of catenarin and erythroglaucin has been made. It involves nuclear oxidation of the corresponding benzoyl benzoic acid. This reaction and the following ring closure give very good yields of catenarin dimethyl ether. Complete demethylation yields catenarin and partial demethylation erythroglaucin which can also be formed by the partial methylation of catenarin.

We are grateful to Prof. J. H. Birkinshaw and Prof. S. Shibata for the kind supply of samples of natural catenarin and erythroglaucin for comparison.

REFERENCES

1. Aghoramurthy, K. and Seshadri, T. R. .. *J. Sci. Industr. Res., India*, 1954, **13A,** 114.
2. Neelakantan, S. and Seshadri, T. R. *Ibid.*, 1960, **19 A**, 71.
3. ———, Rajagopalan, T. R. and Seshadri, T. R. *Proc. Ind. Acad. Sci.*, 1959, **49A,** 234.
4. Charles, J. H. V., Raistrick, H., Robinson, R. and Todd, A. R. *Biochem. J.*, 1933, **27,** 449.
5. Raistrick, H., Robinson, R. and Todd, A. R. *Ibid.*, 1934, **28,** 559.
6. Anslow, W. K. and Raistrick, H. .. *Ibid.*, 1940, **34,** 1124.
7. ———— .. *Ibid.*, 1924, **35,** 1006.
8. Jacobson, R. A. and Adams, R. *J. Amer. Chem. Soc.*, 1924, **46,** 1312.
9. Birkinshaw, J. H. .. *Biochem. J.*, 1955, **59,** 485.

MICROWAVE SPECTRUM OF METHYL AMINE

Part I. Experimental Details and Spectrum of CD_3NH_2

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(Communicated by Putcha Venkateswarlu, F.A.SC.)

Abstract

The microwave spectrum of CD_3NH_2 has been studied in the region 24·9–38 KMc. The general experimental arrangements for observing the lines and measuring their frequencies using known spectral lines as frequency standards are described. About fifty lines are recorded and the lower J and ΔJ values for some of these lines have been assigned. The transition $J = 0_{00} - 1_{01}$ has been identified and found to be a doublet with the components at 36,436·8 Mc./sec. and 36,436·2 Mc./sec.

Introduction

The microwave spectrum of CH_3NH_2 has been studied earlier by Hershberger and Turkevitch,[1] Shimoda and Nishikawa[2] in the region 15 to 27 KMc./sec. Later, Shimoda *et al.*[3] obtained the spectrum in the region 7 to 30 KMc./sec. Independently Lide[4] also studied the spectrum of CH_3NH_2 in the region 11 to 38 KMc./sec. Since then the spectrum was extended up to 50 KMc./sec. by Venkateswarlu[5] and Nishikawa.[6] The spectrum of CD_3ND_2 has been obtained recently by Lide[7] in the region 22 to 32 KMc./sec. The microwave spectrum of CH_3ND_2 and CD_3NH_2 are not reported in the literature. It is expected that a study of the microwave spectra of the above two isotopic species along with the known spectral data on CD_3ND_2 and CH_3NH_2 will throw more light on the structure of the molecule and the involved internal motions. A systematic study of these isotopic species CD_3NH_2 and CH_3ND_2 has been undertaken in this laboratory along with a reinvestigation of the spectra of CD_3ND_2 and CH_3NH_2. The present paper deals with the general experimental details and the spectrum of CD_3NH_2. The spectra of the other isotopic species and the discussion on molecular structure will be taken up in later papers.

Experimental Details

A 100 Kc. Stark modulation spectrograph[8] has been set up for this purpose. The spectrograph consists of a 10½ ft. X-band copper absorption

cell. The frequency region 22 to 39 KMc./sec. has been covered by Raytheon klystrons, QK–292, QK–291, QK–290, QK–289, QK–288 and QK–463. A 100 Kc. square-wave modulation of variable voltage 0–1,200 V. is applied to the central electrode. The square-wave generator suitable for this modulation was originally designed by L. C. Hedrik.[9] The one that was used is a modification of the original instrument purchased commercially. This instrument was designed to yield a maximum voltage of 1,200 V. across a cell having a capacity not greater than 1,000 mmfd. and the square-wave is automatically zero based at all voltages. After transmission through the cell the microwave power is rectified by a crystal detector. Sylvania IN 26 crystals were used for the region 22–26 KMc./sec. and IN 53 crystals for the region 26–39 KMc./sec. The crystal output was fed to a low frequency receiver (National HRO-60) tuned to 100 Kc. The output of the receiver was displayed on an oscilloscope (Dumont-304 A or 322). In order to resolve the precise structure of Stark patterns an automatic recording spectrograph[8] was used. In this set-up the klystron was tuned mechanically by motor assembly. The crystal output was fed to a Lock-in-amplifier tuned to 100 Kc. which is coupled to a phase shifter. The output of the Lock-in-amplifier was recorded on an Esterline Angus D.C. milliammeter recorder.

Measurement of frequencies.—Frequencies of the lines were first measured roughly by using different suitable cavity wavemeters for different regions. A PRD type 568B was used for the region 18–22 KMc./sec. Sperry types 349 A and 350 A were used for the regions 19–26 KMc./sec. and 26-39 KMc./sec. respectively. Precise frequency measurements were made by using frequencies of known spectral lines or their harmonics as secondary standards. The experimental arrangement for measurement of frequencies in the region 36–44 KMc./sec., where the first harmonic frequencies of appropriate spectral lines in the region 18–22 KMc./sec. were used as secondary standards, is shown in Fig. 1. Here a K-I band multiplier using a slotted IN26 crystal or a K-J band multiplier using a PRD modified IN26 crystal has been used for harmonic production. In this arrangement two spectrographs are used together simultaneously. Spectrograph A consists of a 3 ft. coin silver K-band Stark cell and is used for observing the known standard lines and may be called a secondary standard spectrograph. After setting the klystron of the secondary standard spectrograph for the frequency of the proper standard line the sawtooth sweep of the klystron is removed. Spectrograph B which may be called the search spectrograph is used for observing new lines and its description has been given earlier. A small amount of power from klystron 1 is taken through a Tee and its frequency is doubled by a crystal multiplier. The harmonic frequency is then mixed with a small

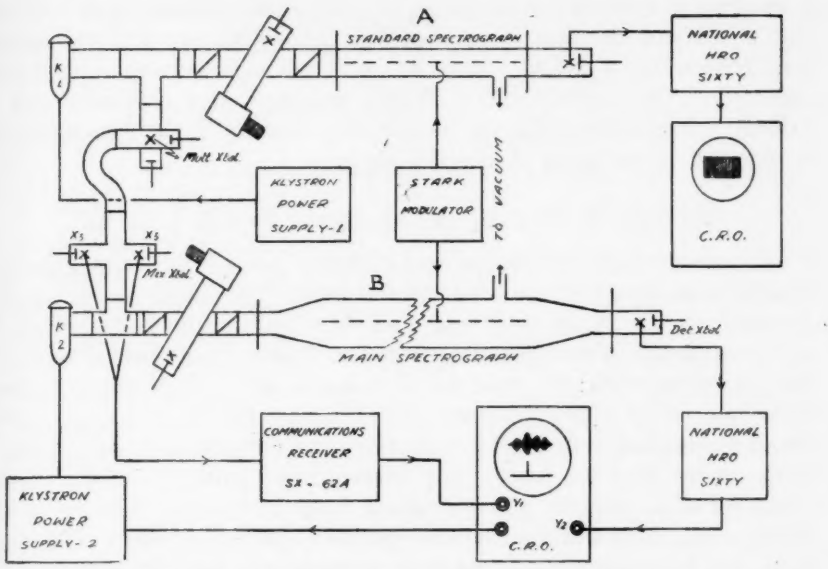

FIG. 1. Block diagram of the experimental arrangement for measurement of the microwave spectral lines in the region 36–40 KMc./sec.

amount of power from 2 through a magic tee. Crystal mixers X_3 are connected to the opposite arms 2 and 3 of the magic tee. The use of the magic tee helps to have a balanced mixer as well as to isolate the klystrons. For measurement of frequencies in the region 18–36 KMc./sec., where frequencies of appropriate spectral lines in this region are taken as secondary standards, a small amount of power from klystron 1 is directly mixed without multiplication, with small amount of power from klystron 2 through a magic tee and necessary directional couplers. The resulting beat frequencies from the crystal mixers X_3 are fed into a communications receiver (Hallicrafters type SX-62 *a*). The output of the receiver is displayed on a double beam oscilloscope (Dumont 322) along with the line to be measured. The receiver output appears as a marker whenever one of the beat frequencies from the mixers X_3 corresponds to the frequency to which the communications receiver is tuned. The receiver setting is adjusted so that the marker coincides with the centre of the search line. In this way the beat frequencies between the two oscillators, one of which is stabilised at the frequency of the known line (within the range of about 110 Mc. from the search line) while the other at the line to be measured, are measured. Whenever it was necessary to extend the frequency range of the measurements with respect to the frequency of

a standard absorption line an output of a r.f. signal generator (GR 1,001 A) was mixed with the beat frequencies from mixers X_3. In this way known lines lying within $\pm$ 215 Mc. from the search line could be used as secondary standards. The receiver and the signal generator were calibrated with a GR-620 A heterodyne frequency meter. The accuracy of the lines measured is expected to be better than $\pm$ 0·5 Mc./sec.

SPECTRUM OF CD_3NH_2 IN THE REGION 24·9-38 KMC./SEC.

The spectrum of CD_3NH_2 has been studied in the region 24·9-38 KMc./sec. and fifty lines have been recorded and measured. The sample has been kindly provided by Dr. A. P. Gray and Prof. R. C. Lord who have published[10] earlier the details of the chemical preparation. The observed lines can be classified into three kinds: (1) those that show first order Stark pattern, (2) those that show second order Stark pattern and (3) those that show a Stark pattern which is a mixture of first and second orders. All the lines are listed in Table I. Some of the lines are having well resolved Stark patterns and their lower J and $\triangle$J values could be well ascertained from the relative intensities of the Stark components and their relative mutual separations.[11, 12, 13] For those lines, that have partially resolved Stark patterns, only the limit of the J value could be set. Finally there are a number of lines with unresolved Stark patterns.

The lines at 36436·2 Mc. and 36436·8 Mc./sec., shown in Fig. 2, are identified as belonging to the transition $J = 0_{00} \rightarrow 1_{01}$. The observed splitting

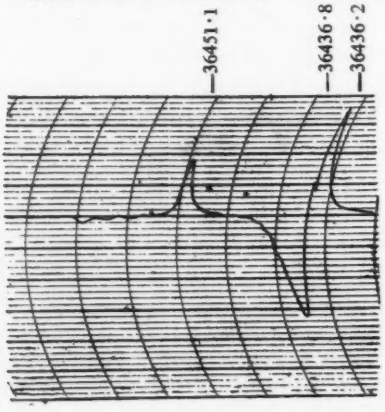

FIG. 2

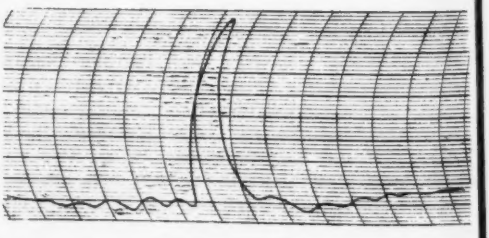

FIG. 3

FIG. 2. $J = 0_{00} - 1_{01}$ line and 36451·1 line showing 4 first order Stark components.
FIG. 3. The line at 34670 Mc. showing 6 first-order Stark components.

TABLE I

Frequency Mc./ Sec.	Intensity	Order of Stark effect	Number of Stark components	Lower J	$\pm \Delta J$
38023·7	M	2	..	..	..
37951·4	S	1	3	3	0
37840·5	W	1	..	..	..
37812·2[a]	M	2	..	..	..
37807·9[a]	M	1	..	..	..
37427·1[b]	M	2	6	6	0
37386·3[c]	M	1	4	4	0
37320·9[d]	S	2	..	..	..
37230±10	W	2	..	..	..
37148±10	W	2	..	..	..
37015·4[e]	M	2	3	3	0
36856·9[f]	M	1 & 2	..	..	..
36816·6	W	1 & 2	..	..	..
36753·7	W	1	..	..	..
36451·1	M	1	4	4	0
36436·8 36436·2	S	2	1	($J = 0_{00} \rightarrow 1_{01}$)	
35590·6 35588·1	S	2	5	5	0
35324·7	M	1 & 2	..	..	..
35202·1	W	1	..	..	..
35171·4[g]	S	1 2	6	6	0
35135·7[h]	S	2	..	..	..
35100*	M	2	..	..	..
34995·0	W	2	..	..	..
34962·4[i]	S	1 & 2	..	..	..
34670*	W	1	6	6	1

TABLE I (*Contd.*)

Frequency Mc./ Sec.	Intensity	Order of Stark effect	Number of Stark components	Lower J	$\pm\Delta J$
34625*	W	1	..	..	..
33900*[j]	W	1	..	..	..
33860*	W	1	..	..	..
33692·1	S	2	..	..	..
33664·2	S	1 & 2	..	..	..
33160·4	M	2	..	..	..
32968·3	W	2	..	..	..
32298·0	W	1	..	..	..
32267·4	S	2	..	..	..
32178·0[k]	W	1 & 2	..	..	..
31933·7[l]	M	1 & 2	..	..	..
31656·2[m]	S	2	3	3	1
31422·9[n]	S	2	..	..	..
30057·2	M	2	..	..	..
30010·5[o]	W	1 & 2	..	..	..
29913·2[p]	S	2	..	..	..
29507·2	M	2	..	..	..
28601·6[q]	S	2	2	2	0
27815·0[r, s]	S	2	2	2	1
27472·5[s]	S	2	..	..	..
25834·5[t]	W	1 & 2	..	..	..
25570·4[u]	W	2	2	2	1
24913·1[v]	W	2	3	3	1

* Frequencies of these lines are measured with wavemeter only.

(*a*) These lines lie close together. A first-order line and a second-order neighbouring one has been observed in many cases.

(*b*) Very likely there are six Stark components. Five components are well seen.

(*c*) There is a weak line on the low frequency side of this line which shows second-order Stark effect.

(*d*) Shows three components the farthest being well separated. The nearest one shows up some unresolved structure at high voltages and probably is a mixture of some components. It appears that the total number of components is probably more than five or six and $\Delta J = 0$, but this conclusion is not definite.

(*e*) Has a neighbouring line on the low frequency side showing first-order Stark effect, the Stark pattern for which is not resolved.

(*f*) Shows three first-order Stark components on each side and one more Stark component on high frequency side which is more intense. The strong component at high voltages shows three broad envelopes.

(*g*) The Stark component on the high frequency side resolves into six while the one on the low frequency side stays as one.

(*h*) Three components are seen. Probably there are more. But these are mixed up with a weak second-order line that lies between 35171·4 Mc. and 35135·7 Mc. lines.

(*i*) There are two or three broad envelopes for the Stark pattern on the high frequency side while only one on the low frequency side.

(*j*) Two Stark components on high frequency side seen clearly and only one Stark component is seen on the low frequency side which is mixed up with the Stark component of the 33860 Mc. line. It is not clear whether this line is showing a first-order or a mixture of first and second-order Stark effect.

(*k*) There are two Stark components on each side. But at high voltages the one on the low frequency side goes down gradually and disappears.

(*l*) There is one Stark component on each side at low voltage. At high voltages the one on the high frequency side splits into two while the one on the low frequency side moves towards the main line and slowly disappears.

(*m*) The Stark component nearest to the main line is strongest and probably corresponds to $M = 0,1$. The mutual separation increases for the component away from the main line.

(*n*) Shows three Stark components at 300 V. the nearest one to the main line being the most intense. At 900 volts the intense component begins to show up more components.

(*o*) At low voltages this line shows one Stark component on each side. At high voltages the one on the high frequency side broadens into two envelopes while the one on the low frequency side slowly disappears (probably moves towards the main line).

(*p*) Appears to show four or probably more Stark components, the one away from the zero-field line being more intense. The farthest ones have smaller mutual separations.

(*q*) At low pressures there appears to be a weak main component on the high frequency side. There are two Stark components, the farthest one being more intense. The mutual separation for the two Stark components is more than the separation between the main line and the nearest Stark component.

(*r*) Similar to the line marked *m*.

(*s*) Shows irregularly spaced Stark components. This may be due to superposition of a weak line.

(*t*) There is one Stark component on each side at low voltages. At high voltages the one on the high frequency side appears to split into more than one component and the one on the low frequency side, slowly goes down in intensity like that for the line marked *l*.

(*u*) Similar to the line marked *r*.

(*v*) At 250 volts this line appears to show four Stark components. The farthest one probably corresponds to $M = 0$. At 225 volts this shows three Stark components of which the

farthest one being more intense, probably corresponds to $M = 0, 1$. It looks like $\Delta J = \pm 1$ the lower J being 3, but this cannot be said definitely as there is a weak line superposed on the Stark components.

is probably due to the involved hindered rotations. The line at 36451·1 Mc. in Fig. 2 has four first-order Stark components and the outer components are most intense. The lower J for this transition has been assigned as 4 and ΔJ as 0.

Figure 3 shows a line at 34,670 Mc. with six first-order Stark components. Since the inner components are most intense, the ΔJ for this transition is assigned as ± 1 and the lower J as 6. Figure 4 shows a line at 37,951·4 Mc. with 3 first-order Stark components with lower $J = 3$ and $\Delta J = 0$.

Figure 5 shows the line at 37015·4 with three second-order Stark components. The intensity and the mutual separation for the Stark components

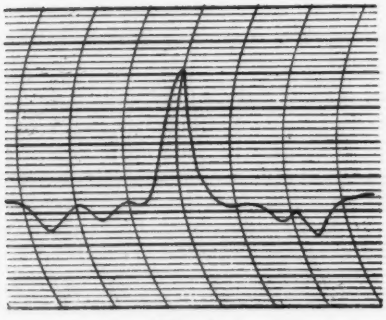

FIG. 4

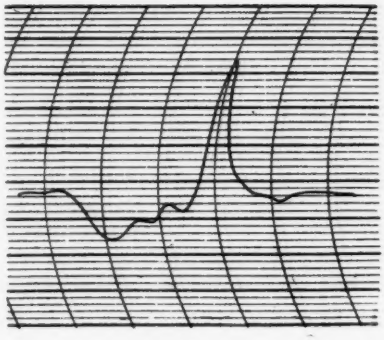

FIG. 5

FIG. 4. The line at 37951·4 showing 3 first-order Stark components.

FIG. 5. The line at 37015·4Mc. showing 3 second-order Stark components.

of this line increases as one goes off from the zero-field line. This suggests that $\Delta J = 0$ for the transition and the lower J as 3.

ACKNOWLEDGEMENTS

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Industrial Research to whom the author is highly thankful for the award of a Fellowship. It has been possible to set up the microwave spectroscopy laboratory with a special grant given to the Department of Physics by the University Grants Commission to whom we are highly thankful.

References

1. Hershberger, W. D. and Turkevitch, J. — *Phys. Rev.*, 1947, **71,** 554.
2. Shimoda, K. and Nishikawa, T. — *J. Phys. Soc. Japan*, 1953, **8,** 133, 425.
3. ——— and Itoh, T. .. *Ibid.*, 1954, **9,** 974.
4. Lide, Jr., D. R. .. *J. Chem. Phys.*, 1952, **20,** 1812; 1953, **21,** 571.
5. Venkateswarlu, P. .. Work to be published.
6. Nishikawa, T. .. *J. Phys. Soc. Japan*, 1957, **12,** 668.
7. Lide, Jr., D. R. .. *J. Chem. Phys.*, 1957, **27,** 343.
8. Gordy, Smith and Trambarulo .. *Microwave Spectroscopy*, John Wiley & Sons Inc., New York, 1952.
9. Hedrik, L. C. .. *Rev. Sci. Instr.*, 1949, **20,** 781; 1951, **22,** 537.
10. Lord, R. C. and Allen, P. Gray — *J. Chem. Phys.*, 1957, **26,** 690.
11. Golden, S. and Wilson, Jr., E. B. — *Ibid.*, 1948, **16,** 669.
12. Hughes, R. H., Good, W. E. and Coles, D. K. — *Phys. Rev.*, 1951, **84,** 95.
13. Townes, C. H. and Schawlow, A. L. .. *Microwave Spectroscopy*, McGraw-Hill Book Co., 1954.

KINETICS OF OXIDATION OF ALCOHOLS BY CHROMIC ACID—THE MECHANISM OF THE REACTION

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(Contribution from the Department of Chemistry, Madras Christian College, Tambaram)

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Introduction

Oxidations of a variety of organic compounds by chromic acid have been extensively studied and the generally accepted mechanism is the one put forward by Westheimer.[9] Using isopropyl alcohol as the substrate, the main features of the mechanism involved as an essential part, the rapid formation of an ester—an alkyl chromate, followed by interaction with a base, water playing this role, in the slow rate-determining step. Using deuterated compounds, Westheimer also showed that the rate-determining step involved the removal of the C—H hydrogen in the part carrying the alcohol group. Further, it was considered that in the last step, the chromium was reduced to the tetravalent state while the hydrogen was removed as a proton.

While the rupture of the C—H bond appears to be on fairly certain ground, it appeared worth while to investigate the problem further. In two preliminary communications[1 a–b] we had indicated the complex nature of the reaction and the difficulties in the Westheimer mechanism and in a further detailed study, one of us had presented the results with a group of aliphatic secondary alcohols.[8 a] In the present communication we are presenting the essential results for elucidating the mechanism of the reaction and a tentative mechanism is also proposed. We have to refer in this connection also to the publications of Roček[6] which represent a different point of view from that of Westheimer.

The Formation of a Chromate Ester

The evidence in favour of the formation of an ester as a step in the reaction is based on its isolation in benzene solution as a transient compound.[9 a–b] Generally it is found that esterification involves an activation energy of the order of 13 K. calories or more while the apparent activation energy is very much lower in the present case. Further, esterification

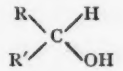
of secondary butyl alcohol involves a higher activation energy than isopropyl alcohol[4a] while we find a lower activation energy for the oxidation of the secondary butyl compound.[8a] Similarly the rates of hydrolysis of the sec. butyl esters are consistently slower than those of the corresponding isopropyl esters.[7] On both grounds we are forced to the conclusion that the formation of a chromate ester cannot be an essential step in the oxidation reaction and any mechanism proposed has to deal only with the two reactants independently.

The Rupture of the C—H Bond in the C—H (OH) Group

As indicated earlier, Westheimer has demonstrated that the rate-determining step involved a rupture of the C—H bond with the removal of the hydrogen atom as a proton. While we can accept the first part, we find it difficult on the evidence available to accept the second part. Roček (*loc. cit.*) in his mechanism has left the question open. The study of a series of compounds with a systematic variation in the structure as well as a graded system of solvent mixtures was expected to provide some of the information required. For our purpose, it is adequate to consider only the Arrhenius activation energies and the rate constants at any one temperature. These are presented in Tables I and II.

Table I

Activation energies in the oxidation of secondary alcohols



by chromic acid in 50% acetic acid and the Arrhenius Pre-exponential factor

R	R′	E_A (kilocalories)	$Log_{10}PZ$	$k_2 \times 10^4$ at 50° C.
Me	Me	14·31	5·57	0·7800
Me	Et	13·54	5·29	1·3620
Me	n–Pr	13·45	5·37	1·8810
Me	Ph	14·18	6·28	4·8420
Ph	Ph	13·50	6·22	11·750

It will be noticed that with increasing electron release by a substituent group, activation energy for the reaction progressively gets reduced and the

TABLE II

Rate constants ($10^4 k_2$) *in acetic acid-water mixture at* 40° *C.*

Alcohol	Volume % acetic acid in medium					
	30	40	50	60	70	80
Isopropyl ..	0·098	0·198	0·390	0·835	1·90	..
Sec-butyl ..	0·172	0·345	0·715	1·445	3·47	..
Alpha-phenyl ethyl ..	..	..	2·42	4·61	10·1	23·2
Benzhydrol ..	..	..	6·03	8·64	18·2	50·1
Fluorenol–9 ..	..	..	9·42	18·0	38·3	76·7

trend of rate constants follows the trend of resonance stabilisation of a carbonium ion. The influence of the environment by change to conditions of lower water content which favours a stabilisation of any carbonium ion intermediate is also in the right direction. This necessarily implies that in the rate-determining step the hydrogen transfer is essentially a hydride ion transfer. Lewis and Symons[3] in analysing various aspects of rupture of a C—H bond arrive at a conclusion that electron repelling groups by their inductive effect facilitate such transfers and the reaction between triphenylmethyl cation and isopropyl alcohol studied by Bartlett and McCollum[2] bears out such group influence.

THE INFLUENCE OF PRODUCTS OF THE REACTION AND OF IONIC STRENGTH ON THE OXIDATION REACTION

In every instance, the addition of the ketone formed by the oxidation had no influence on the rate and the changes in ionic strength of the medium by suitable additions of different acetates had no appreciable effect. On the other hand, the addition of tervalent chromium had a definite retarding influence though the reduction appears to be small (Table III) (Roček, *loc. cit*).

The only addition that appears to have any pronounced influence is thus the chromium ion and the change in rate constant appears to be proportional to the square-root of the chromium ion concentration.

In support of the postulated mechanism, Westheimer[9a] has reported that the addition of a base like pyridine catalyses the oxidation. It will be

TABLE III

Effect of change in ionic strength on the oxidation of isopropyl alcohol by chromic acid in sulphuric acid (Roček and Krupička, loc. cit.)

Temp.: 25° C. Concentrations: $HClO_4$ 0·0046 M; CrO_3 0·0002 M; Iso-propylalcohol 0·2600 M. Rate constants × 10^6

Salt added	Concentrations		
	0·04 M	0·08 M	0·26 M
$NaClO_4$ ..	1·6	1·5	1·3
Pyridinium perchlorate ..	1·7	1·6	1·45
Trimethyl ammonium perchlorate ..	1·6	1·4	..
None ..	2.0	..	..

TABLE IV

Influence of products of the reaction and added ions on the oxidation of dl-*alphaphenyl ethyl alcohol in 70% acetic acid at 45° C.*

Compound added	Concentration Moles	$k_2 \times 10^4$	
None ..	..	13·75	(18·49 at 50° C.)
Calcium Acetate ..	0·00505	13·02	..
Aluminium Acetate ..	0·00505	13·14	..
Chromium Acetate ..	0·00300	12·10	..
	0·00505	11·75	..
	0·00666	11·30	..
	0·01135	10·80	..
Acetophenone ..	0·03614	18·52	at 50° C.

noticed from the data of Roĉek (*loc. cit.*) that there is room for a difference of opinion. We are unable to confirm Westheimer's catalysis by pyridine. The influence if any is slight and then it is one of retardation, not acceleration.

TABLE V

Influence of pyridine on the oxidation of alcohols by chromic acid in 70% acetic acid at 50° C.

Alcohol		Concentration of pyridine added	$k_2 \times 10^5$
Isopropyl alcohol	..	Nil	40·37
	..	0·00689 M	40·03
	..	0·01767 M	38·86
	..	0·03203 M	38·24
α-phenyl	..	Nil	184·9
ethyl alcohol	..	0·01937 M	181·9

RETARDING INFLUENCE OF ADDED OXIDISABLE IONS

It is generally observed that the commonest oxidations involve only a one-electron transfer though instances are not wanting where the change involves a two-electron transfer. The two-electron process is invariably associated with considerable dislocations in the co-ordination sphere. In the present studies the starting material is chromic acid or the acid chromate ion while the end product is the tervalent chromium ion in a solvated condition. We have thus a change from tetrahedral disposition of atoms to an octahedral distribution of the solvent molecules or of water. A change involving two-electron transfer is thus a possibility. Westheimer's technique of determining the induction factor by the addition of manganous ions is a convenient test while tervalent cerium is also an equally useful tool. Under the conditions indicated by Westheimer, manganese should be precipitated as MnO_2 but in our case it remains wholly in solution, any tetravalent manganese being kept as an acetate complex. The rate determinations are to some extent rendered less accurate on this account. This difficulty is however not present with the cerium compound. The addition of a manganous

compound reduces the rate to $\frac{1}{3}$ of the value while that of cerium reduces it to $\frac{1}{2}$. (Table VI).

TABLE VI

Oxidation of isopropyl alcohol at 50° *C.* (0·02 *M*)

Solvent composition % Acetic acid by volume	Second order rate constants × 10^5		
	Absence of Mn^{++} or Ce^{+++}	In presence of Ce^{+++} 0·00293 M	In presence of Mn^{++} 0·00293 M
70	40·37	21·02	13·80
50	7·80	4·05	2·67

It is thus clear that the rate-determining step in the reaction involves a two-electron transfer.

THE MECHANISM OF THE OXIDATION REACTION

Any mechanism that can be postulated for the reaction has thus to take into account the following factors:—

(i) The rate-determining step involves a hydride transfer.

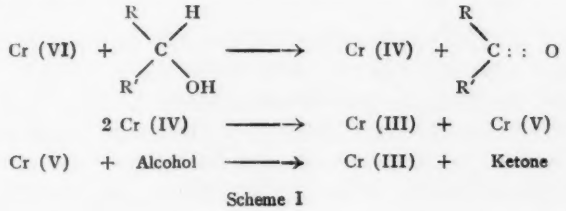
(ii) The rate-determining step involves a two-electron transfer.

(iii) The reaction is facilitated by inductive electron release in the alcohol.

(iv) Decrease of water content increases the reaction rate.

(v) Tervalent chromium has a retarding influence.

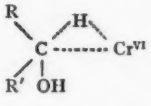
Two alternative schemes can be proposed for the purpose as follows:—



Scheme I

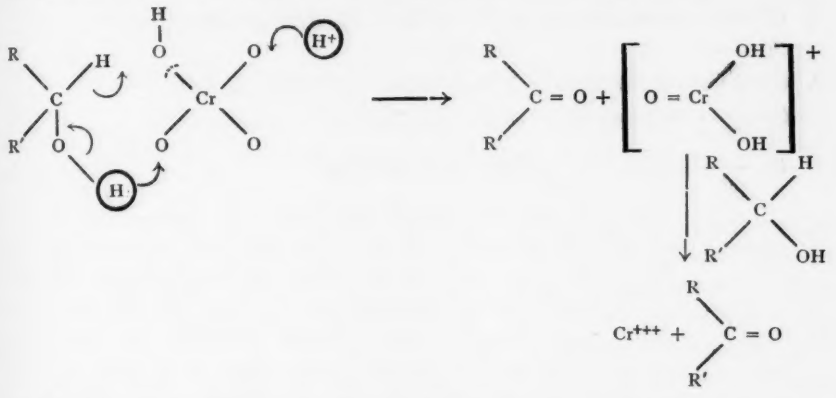
Scheme II

Dielectric constant values for the different solvent mixtures used in the study were not available but assuming an approximate validity of the mixture law, it was observed[8b] that there is a linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant. The mechanism has then to be visualised as an ion-dipole reaction and the removal of the hydride ion has to be a stage after the formation of the transition state. We have ample evidence to support the participation of Cr (V) in oxidations. Mosher and his associates have shown that alcohol oxidations can be effected by this transient body.[5] An interesting feature of his study is the postulate of the cation $HCrO_3^+$ as the reacting ion in chromic acid solutions and Roček also has postulated this species in the oxidation of hydrocarbons.[6 b] While one cannot rule out the possibility of the presence of this cation in glacial acetic acid and in solutions with a higher proportion of this component in the solvent mixtures, it is doubtful if any appreciable concentration of the cation can exist in the more aqueous systems. In our view, evidence is as yet inadequate to decide among the various alternative oxidising species but we can be fairly certain about the valence state of the oxidiser. The comparatively small effect of the changes in ionic strength suggests a transition state of the following type followed by a rapid abstraction of the hydroxyl hydrogen along with the transfer of the hydride ion in the next and final stage of the reaction. Of the two alternative modes



of removal of tetravalent chromium, we consider that meachanism I is the more probable. Disproportionation of a less stable form to a higher and lower state of oxidation has several analogies in the fifth, sixth and seventh groups in the periodic table and it is only in mechanism I where the formation of Cr (V) from Cr (IV) can be retarded by the presence of Cr (III). The retardation of the reaction by tervalent chromium that we find can thus be held to favour this view. Other techniques than simple rate studies are

obviously necessary for a positive identification of the transient reactive intermediate species. Apparently a cyclic process nearer the Roček mechanism is to be preferred to the Westheimer mechanism for these oxidations:—



Further work in progress in these laboratories may be expected to give a clearer picture.

Summary

An analysis of the various factors affecting the oxidation of secondary alcohols by chromic acid in aqueous acetic acid systems shows the following features. The formation of an ester of chromic acid is not essential to oxidation. Both structural and solvent influences from the study of a series of secondary alcohols, aliphatic as well as aromatic, suggest that in the rate-determining step of the reaction the C—H hydrogen is removed as a hydride ion. The rate-determining step involves a two-electron transfer and the reacting species can be hexavalent and pentavalent chromium. A tentative mechanism of the reaction has been suggested incorporating these features.

References

1. (*a*) Anantakrishnan and Venkatasubramanian .. *Curr. Sci.*, 1958, **27**, 438.
   (*b*) ———— .. *Ibid.*, 1959, **28**, 325.
2. Bartlett and McCollum .. *J. Amer. Chem. Soc.*, 1956, **78**, 1441.
3. Lewis and Symons .. *Quarterly Reviews*, 1958, **12**, 245.
4. Moelwyn Hughes .. "*Kinetics of Reactions in Solutions*," Oxford, 1947.
5. Mosher *et al.* .. *J. Amer. Chem. Soc.*, 1948, **70**, 2544; *Ibid.*, 1949, **71**, 2 86; *Ibid.*, 1950, **72**, 4452; *Ibid.*, 1951, **73**, 1302.

6. (*a*) Roček and Krupička .. *Coll. czech. Chem. Comm.*, 1958, **23**, 2068.
(*b*) ———— .. *Ibid.*, 1957, **22**, 1509.
7. Smith and Olson .. *Z. Physik. Chem.*, 1925, **118**, 99.
8. (*a*) Venkatasubramanian .. *Proc. Ind. Acad. Sci.*, 1959, **50**, 156.
(*b*) ———— .. Unpublished work.
9. (*a*) Westheimer and Cohen *J. Amer. Chem. Soc.*, 1952, **74**, 4387.
(*b*) ———, Holloway and Cohen *Ibid.*, 1951, **73**, 65.
(*c*) ——— and Leo .. *Ibid.*, 1952, **74**, 4385.

ULTRAVIOLET ABSORPTION SPECTRA OF DIHYDROINDOLE ALKALOIDS

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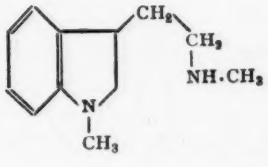
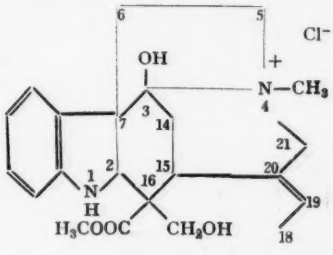
It is well known that alkaloids having the dihydroindole chromophore exhibit in neutral solution, absorption maxima near about 250 and 300 mμ. Hodson and Smith[1] have observed that the nature of the spectra of these alkaloids in acid solution is dependent on the number of carbon atoms separating N_a and N_b. Thus the absorption maxima of eserine-type compounds undergo a hypsochromic shift of about 10 mμ on addition of acid, while those of hexahydro-β-carbolines are unchanged. The indoline absorption of compound (I) in which N_a and N_b are separated by more than three carbon atoms undergoes a dramatic change to benzenoid absorption on addition of acid. Bearing these observations in mind, it was proposed[2-3] on the basis of ultraviolet absorption characteristics that echitamine contained a N_a–C–N_b system. Some further degradation experiments[4] also appeared to support this proposal. Recently, Conroy and co-workers[5] have proposed structure (II) for echitamine chloride, which satisfactorily explains all the experimental data, with the exception of u.v. absorption



I



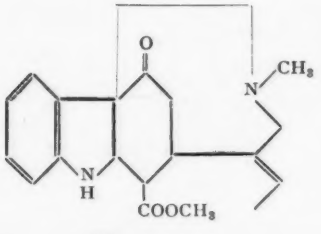
II

characteristics. Echitamine chloride shows only indoline absorption even in strong acid and this has been attributed to steric hindrance to protonation at N_a. It was therefore of interest to examine the u.v. spectra of several products derived from echitamine (Table I) and some other dihydroindole alkaloids in acid solution.

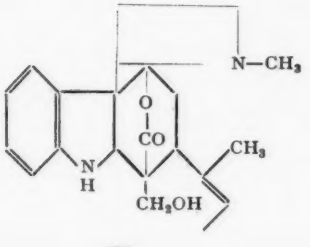
TABLE I

	Compound	Substituents at C_{16}		u.v. in 0·1 N acid	u.v. in 5 N acid
1.	Echitamine ..	CO_2CH_3,	CH_2OH	Indoline	Indoline
2.	Echitinolide ..	COO– ,	CH_2OH	,,	,,
3.	Lithium aluminium hydride reduction product of echitinolide	CH_2OH,	CH_2OH	,,	,,
4.	Alloechitamine[5] ..	H,	CO_2CH_3	,,	Benzenoid
5.	Lithium aluminium hydride reduction product of alloechitamine	H,	CH_2OH	Benzenoid	..
6.	Hemitoxiferine-I[6] ..	H,	–CH(OH)–O–	,,	..

It is seen from the data recorded that ultraviolet absorption behaviour of compounds of the N_a-C-C-C-N_b type (β-indole type alkaloids) is dependent on the number and nature of the substituents at C_{16} and also on the strength of the acid. For example, while alloechitamine (III) exhibits indoline absorption in 0·1 N HCl, and benzenoid absorption in 5 N HCl, the corresponding lithium aluminium hydride reduction product exhibits only benzenoid absorption even in 0·1 N acid. Compounds of the type of



III



IV

echitinolide (IV) and its lithium aluminium hydride reduction product, bearing two substituents at C_{16} exhibit only indoline absorption in 5 N acid.

Ajmaline in which N_a and N_b are separated by only two carbon atoms, shows indoline absorption in 0·1 N acid and benzenoid absorption in 5 N acid. Finally, calycanthine[7] in which N_a and N_b are separated by a single carbon atom exhibits indoline absorption even in strong acid.

The ability of N_a to protonate in dihydroindole alkaloids, with consequent change to benzenoid absorption, appears therefore to be influenced not only by the distance from N_b, but also on the degree and nature of substitution in the neighbourhood of N_a.

Summary

The ease of protonation of N_a of dihydroindole alkaloids is shown to depend not only on the distance from N_b, but also on the degree and nature of substitution in the neighbourhood of N_a, from a study of their u.v. spectra in acid solution.

Acknowledgement

We are grateful to Dr. R. H. Manske and Prof. Asima Chatterjee for samples of calycanthine and ajmaline respectively, and to Dr. H. Conroy for a copy of the paper on echitamine in advance of publication. We thank the Council of Scientific and Industrial Research for the award of a Senior Research Fellowship (to S. R.).

References

1. Hodson and Smith .. *J. Chem. Soc.*, 1957, 1877.
2. Govindachari and Rajappa *Proc. Chem. Soc.*, 1959, 134.
3. Birch, Hodson and Smith .. *Ibid.*, 1959, 224.
4. Govindachari and Rajappa *Chem. and Ind.*, 1959, 1549.
5. Conroy, Bernasconi, Brook, Ikan, Kurtz and Robinson *Tetrahedron Letters*, 1960, No. 6, 1.
6. Battersby and Hodson .. *Proc. Chem. Soc.*, 1958, 287.
7. Woodward, Yang, Katz, Clark, Harley-Mason, Ingleby and Sheppard *Ibid.*, 1960, 76.

CRYSTALLINE CHEMICAL COMPONENTS OF THE FLOWERS OF *RHODODENDRON NILAGIRICUM* ZENK.

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Plants belonging to the genus *Rhododendron* are considered to be poisonous to cattle.[1] The results of the chemical examination of the leaves of *Rhododendron nilagiricum* Zenk. (Syn. *R. arboreum* Sm. var. *nilagirica* Cl.) have been communicated recently from these laboratories.[2] *Rhododendron* flowers were found to possess insecticidal activity.[3] According to Madden[4] the flowers of *R. arboreum* Sm. are eaten by the local people in some parts of the Himalayas and they become intoxicated if they consume them in large quantities. There is no reference in the published literature to past chemical work on the flowers of *R. nilagiricum*. The results of the chemical examination of the flowers of this plant are described in the present paper.

The air-dried flowers were extracted with petroleumether, ether and methanol in succession. The petroleum-ether extract yielded, besides a large amount of wax, a minute quantity of a crystalline substance. The ether extract yielded quercitrin and ursolic acid as the crystalline components. From the methanolic extract, besides a large amount of resinous material, a small quantity of quercetin could be obtained after hydrolysis with mineral acid; the presence of glucose in the aqueous portion after hydrolysis was shown by the preparation of its osazone and paper chromatography.

Quercitrin is quercetin-3-rhamnoside. Although its occurrence was reported in a wide variety of plants, its isolation has not so far been reported from the genus *Rhododendron*. The isolation of quercitrin from "lemon flavine" obtained from the bark of the black oak in high yield has been described by Booth and DeEds.[5]

The identity of the glycoside obtained in the present investigation as quercitrin has been established by its m.p., analysis, hydrolysis to quercetin and rhamnose and the hydrolysis of the methyl ether to 5:7:3′:4′-0-tetramethyl quercetin (m.p. and mixed m.p. with an authentic sample).

Quercetin was characterized as its acetate (m.p. and mixed m.p.). The nature of the sugar in the original glycoside was established by descending paper chromatography.

Ursolic acid was identified through its physical properties and preparation of its acetate (m.p. and mixed m.p. with an authentic sample).

Experimental

The material used in this investigation was obtained from Ootacamund, Nilgiri Hills in S. India.

The air-dried flowers (500 g.) were extracted with petroleum ether (2×6 l.) in the cold, then with solvent ether (3×4 l.) in the cold and finally with methanol (3×4 l.) by boiling under reflux.

Petroleum ether extract.—On complete removal of the solvent a greenish syrupy residue (6 g.) was obtained which on keeping for two months deposited a small quantity of a crystalline material along with some waxy matter. On warming the residue, the waxy matter melted leaving behind the crystals. The melt was decanted off and the crystals washed with warm petroleum ether. Crystallization from chloroform-benzene gave colourless plates, m.p. 278–80° (Yield: *ca.* 10 mg.). In the Liebermann-Burchard test it gave a red colour slowly changing to pink. Dearth of material prevented further examination of this substance.

Ether extract.—The yellow residue (*ca.* 4 g.) obtained on complete removal of the solvent turned partly crystalline when left for a week. Ether (50 ml.) was added and thoroughly shaken when a portion of the residue went into solution. The ethereal layer was decanted (solution X, *see* later) and the remaining yellow granular powder was again treated with ether (25 ml.). The ethereal layer was decanted and united with the first portion.

The yellow granular residue (1·7 g.) answered the colour reactions for anthoxanthins. Crystallization from dilute alcohol, ethyl acetate-methanol, alcohol-chloroform and dilute alcohol in succession gave yellow needles, m.p. 180–82° (quercitrin) (yield: 0·8 g.) The different melting points reported in the literature for quercitrin vary from 168°[6] to 182–85°[7] [Found on sample dried under high vacuum at 110° for 6 hrs. over phosphorus pentoxide and weighed in a closed pig: C, 56·0; H, 4·3. $C_{21}H_{20}O_{11}$ (quercitrin) requires: C, 56·2; H, 4·5%]. An alcoholic solution gave a deep pink colour with magnesium and hydrochloric acid. A deep green colour was obtained with neutral alcoholic ferric chloride. Molisch's test was positive. A yellow precipitate was obtained with neutral lead acetate

solution. In the test with zirconium oxychloride and citric acid, as described by Hörhammer and Hänsel,[8] a colourless solution was obtained at the end, indicating the absence of a free hydroxyl group in the 3-position.

Methylation of the glycoside.—This was carried out by repeatedly treating an ice-cold absolute alcohol solution of the glycoside with ice-cold ethereal diazomethane until the ferric reaction was negative. Crystallization from absolute alcohol-ether gave colourless needles, m.p. 180–81° [Found on sample dried under high vacuum at 110° for 6 hrs. over phosphorus pentoxide and weighed in a closed pig: C, 60·1; H, 6·2; —OCH_3, 23·9. $C_{25}H_{28}O_{11}$ (tetramethylether of quercitrin) requires: C, 59·5; H, 5·6; —OCH_3 (4), 24·6%].

Hydrolysis of the methylated glycoside.—The above methylated glycoside (40 mg.) was hydrolysed by boiling under reflux with 2% sulphuric acid in 50% alcohol for 1 hr. The reaction mixture was worked up in the usual way. On crystallizing the residue from alcohol yellow needles, m.p. 190–91° were obtained [Found: C, 63·8; H, 5·6. $C_{19}H_{18}O_7$ (quercetin tetramethyl ether) requires: C, 63·7; H, 5·1%]. Mixed m.p. with an authentic sample of 5:7:3′:4′-O-tetramethyl quercetin, obtained from hyperoside[3] was undepressed.

Hydrolysis of the glycoside.—This was carried out by heating the glycoside (85 mg.) with 2% aqueous sulphuric acid (15 ml.) in a boiling water-bath for 1 hr. The resulting suspension was cooled in ice, the crystals that separated were filtered, washed and crystallized from dilute acetone when yellow needles, m.p. 318–20°, were obtained [Found: C, 60·6; H, 3·8. $C_{15}H_{10}O_7$ (quercetin) requires: C, 59·6; H, 3·3%]. It answered the colour reactions described for quercetin.

Identification of the aglycone by descending paper chromatography.—Whatman No. 1 filter-paper was used. Butanol-acetic acid-water (4:1:5 by volume) was employed as the developing solvent. The chromatograms were run for 18 hrs. Comparison was made with quercetin obtained from the leaves of *Rhododendron falconeri* Hook.[9] Mixed chromatograms were also run. The spots were located by observing under ultraviolet light when they were seen as bright yellow spots with green fluorescence. The aglycone under question and the authentic sample moved through the same distance in individual chromatograms. No separation was observed in mixed chromatograms.

The acetate of the aglycone (prepared using acetic anhydride and sodium acetate) crystallized from alcohol as colourless needles, m.p. 197–98°

[Found: C, 59·1; H, 4·4. $C_{25}H_{20}O_{12}$ (quercetin penta-acetate) requires: C, 58·6; H, 3·9%]. Mixed m.p. with quercetin penta-acetate from the leaves of *Rhododendron falconeri* (*loc. cit.*) was undepressed.

Identification of the sugar.—The acidic filtrate obtained after removing the aglycone from the hydrolysis of the original glycoside was neutralized with freshly precipitated barium carbonate. The suspension was filtered and the filtrate was worked up in the usual manner to get the sugar (syrup) which was identified by descending paper chromatography. Whatman No. 1 filter-paper was used. Butanol-acetic acid-water (4: 1: 5 by volume) was employed as the irrigating solvent and aniline hydrogen phthalate as the spray reagent.[10] Direct comparison of the sugar in question with authentic D-glucose, D-galactose and L-rhamnose showed that the sugar in question might be L-rhamnose. A mixed chromatogram of the unknown with L-rhamnose confirmed the identity.

Treatment of ether solubles of the residue from ether extract (referred to earlier as solution X).—Complete removal of the solvent gave an almost colourless residue which on crystallization from alcohol yielded a colourless powder, m.p. 210–25° (2 g.). The substance was dissolved in hot benzene-methanol (1: 1, 200 ml.) and diluted with water (100 ml.) resulting in the separation of two layers. The lower aqueous-methanol layer was separated, extracted with ether (3×100 ml.) and the extracts were united with the benzene phase. The benzene-ether solution was shaken with 2% sodium hydroxide solution when a precipitate separated at the interphase. This was filtered and washed with water. The precipitate, the filtered alkaline solution and the organic solvent layer were worked up separately as described below.

The precipitate was dissolved in hot methanol and decomposed with hydrochloric acid (1: 1). The resulting suspension was concentrated to a low volume, cooled and the precipitate filtered and washed. Crystallization twice from alcohol yielded colourless needles, m.p. 280–82° (ursolic acid) (yield: 0·8 g.). $[\alpha]_D^{29} = +67{\cdot}2° \pm 3°$ ($c = 0{\cdot}792$ in absolute alcohol) [Found: C, 79·0; H, 11·2. $C_{30}H_{48}O_3$ (ursolic acid) requires: C, 78·9; H, 10·6%]. In the Liebermann-Burchard reaction it gave a red colour changing to violet, then blue and finally green. Mixed m.p. with ursolic acid obtained from the leaves of *R. nilagiricum* Zenk. (*loc. cit.*) was undepressed.

The acetate crystallized from alcohol as colourless needles, m.p. 282–84°. $[\alpha]_D^{30} = +62{\cdot}9° \pm 3°$ ($c = 0{\cdot}983$ in chloroform). [Found: C, 76·9;

H, 10·5. $C_{32}H_{50}O_4$ (ursolic acid acetate) requires: C, 77·1; H, 10·1%]. Mixed m.p. with an authentic sample of ursolic acid acetate was undepressed.

No worthwhile residue was obtained by neutralizing the alkaline filtrate and extracting with ether.

The organic solvent layer was washed with water till neutral, dried and the solvents removed, when a colourless residue (0·22 g.) was obtained. This was found to be mostly waxy in nature. Chromatography over alumina yielded a small quantity (*ca.* 10 mg.) of a colourless substance (nodules), m.p. 255–60°, which was not examined further.

Methanol extract.—Concentration to 400 ml. and leaving in the ice-chest for a month led to the deposition of greenish sticky matter. The solution was decanted and filtered. The filtrate was concentrated under reduced pressure with occasional addition of water and the resulting solution left in the ice-chest. The clear deep red liquid (200 ml.) was decanted from the resin that had again deposited, diluted with an equal volume of alcohol and sufficient concentrated sulphuric acid was added to give a 7% concentration of the acid. The solution was boiled under reflux for 2 hours. Water was added and the alcohol was removed under reduced pressure. The resulting suspension was cooled and extracted with ether. The ethereal extract was washed with water till neutral, dried and the solvent removed. Repeated crystallization of the residue from dilute acetone yielded yellow needles, m.p. 300–06° (0·3 g.). The colour reactions were identical with those answered by quercetin. No separation was observed when mixed chromatograms were run with authentic quercetin as described under the aglycone of the glycoside.

The acetate (colourless needles from alcohol) melted at 192–94° and the mixed m.p. with authentic quercetin penta-acetate was undepressed.

The acidic aqueous suspension left after ether extraction was filtered. The brown residue that was obtained was washed and dried (15 g.). It did not melt below 350° and could not be crystallized from any solvent or solvent mixtures. The clear aqueous filtrate was neutralized with barium carbonate, filtered and the filtrate concentrated under reduced pressure when a large quantity of a syrupy residue was obtained (*ca.* 50 g.). A portion of the residue was dissolved in water, filtered through a bed of charcoal and the filtrate again reduced to a syrup. It yielded an osazone (yellow needles from dilute alcohol), m.p. 207–08°. Mixed m.p. with an authentic sample of D-glucosazone was undepressed.

The sugar was further identified as glucose by descending paper chromatography using butanol-acetic acid-water as the irrigating solvent and aniline hydrogen phthalate as the spray reagent.

Summary

The flowers of *Rhododendron nilagiricum* Zenk. have been examined for their crystalline components by extraction with organic solvents and fractionation along usual lines. Quercitrin and ursolic acid could be isolated as such and quercetin after hydrolysis of one of the crude fractions.

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References

1. Chopra, R. N., Badhwar, R. L. and Ghosh, S. — *Poisonous Plants of India*, Manager of Publications, Delhi, 1949, **1**, 608.
2. Rangaswami, S. and Sambamurthy, K. — *Proc. Ind. Acad. Sci.*, 1959, **50 A**, 366.
3. Tattersfield, F. *et al.* .. *Kew Bull.* (London), 1948, No. **3**, 329; taken from *Chem. Abs.*, 1949, **43**, 3556.
4. *See* Chopra, R. N., Badhwar, R. L. and Ghosh, S. — *Poisonous Plants of India*, Manager of Publications, Delhi, 1949, **1**, 610.
5. Booth, A. N. and DeEds, F. — *J. Am. Pharm. Assocn. Sci. ed.*, 1951, **40**, 384.
6. Rosenthaler, L. .. *Der Nachweis Organischer Verbindungen*, Enke, Stuttgart, 1914, p. 813.
7. Hörhammer, L. and Rao, S. B. — *Arch. Pharm.*, 1954, **287**, 34.
8. ——— and Hänsel, R. .. *Ibid.*, 1953, **286**, 425.
9. Rangaswami, S. and Sambamurthy, K. — *Proc. Ind. Acad. Sci.*, 1957, **46 A**, 245.
10. Partridge, S. M. .. *Nature*, 1949, **164**, 443.

RAMAN SPECTRA OF SINGLE CRYSTALS OF DICARBOXYLIC ACIDS

Part I. β-Malonic Acid and β-Succinic Acid

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1. INTRODUCTION

SATURATED dicarboxylic acids form a series of interesting compounds, since many of their physical properties exhibit oscillatory behaviour with increase in number of carbon atoms. Some of these acids also exhibit polymorphism. Malonic acid and succinic acid are the second and third members of the series. Both of them being transparent to ultra-violet, their Raman spectra have been investigated in single crystal-β-forms, using λ 2537 excitation. Interesting results are obtained which are presented here.

Raman spectra of crystalline malonic and succinic acids were recorded using visible excitation by Anand (1936) who reported only few internal frequencies in each case. Edsall (1937) and Peyches (1934) recorded the spectra of the respective acids in aqueous solutions. Recently the Raman spectrum of succinic acid in powder form has been photographed by R. Theimer and O. Theimer (1950) who reported the existence of seventeen internal frequencies. Data on the Raman spectra of these acids are not complete.

2. EXPERIMENTAL DETAILS

Single crystals of malonic and succinic acids were grown from aqueous solutions of the pure substances by the method of slow evaporation. Under these conditions only the β-form of the two crystals were obtained. Crystals of β-malonic acid were in the form of thick plates, whereas those of β-succinic acid were in the form of needles with their axes parallel to the *c*-direction. Single crystals of both these acids were not completely free of inclusions. Also on continued exposure to the ultra-violet radiation the crystals became opaque and fresh specimens had to be used every two hours. Employing a medium quartz spectrograph and a slit width of 0·025 mm. fairly intense photographs were obtained with exposures of the order of six hours,

3. Results

Photographs of the Raman spectra of β-malonic acid and β-succinic acid are reproduced in Figs. 1 and 2 on Plates VII and VIII. Their respective microphotometer records are also included. The observed frequency shifts in wave numbers have also been marked in figures. The internal frequencies have been tabulated in Table I and the lattice frequencies appearing in low frequency region are included in Table II. In the case of succinic acid the frequencies reported by R. Theimer and O. Theimer are given in Table I. The entire lattice spectrum and many internal frequencies have been recorded by the author for the first time in both the crystals. The Raman lines of succinic acid reported by the above-mentioned authors have all been confirmed except the very faint ones. The Raman frequencies of crystalline oxalic acid recorded by Marignan and Bardet (1952) are also shown in the tables. The infra-red absorption frequencies of malonic and succinic acids compiled from the values reported by Wehrli (1941), Fichter (1940), Hadzi and Sheppard (1953), Flett (1951), Lord and Merrifield (1953) are presented in Table I.

4. Discussion

(*a*) *Internal frequencies.*—The assignments of the Raman lines to the internal oscillations have been indicated in the last column of Table I. Flett (1951), Lord and Merrifield (1953) have reported a large number of infra-red absorption maxima in these acids in the 2500–2700 and 2500–3000 cm.$^{-1}$ regions respectively, which they have attributed to O–H oscillations the frequencies of which have been lowered due to hydrogen bond formation. It is to be noted that only a single frequency at 2880 cm.$^{-1}$ in malonic acid and two frequencies at 2590 and 2835 cm.$^{-1}$ in succinic acid are recorded in Raman effect. These may, following the same reasoning, be attributed to O–H and used to assess the strength of the hydrogen bond. It is well known that the frequencies in the 1400 cm.$^{-1}$ region are the most difficult to identify in the spectra of those molecules which have CH_2 groups adjacent to the acid group. This is mainly due to the superposition of COOH and CH_2 frequencies on one another. Hadzi and Sheppard (1953) have assigned the observed infra-red absorption maxima at 1437 and 1417 cm.$^{-1}$ in the two acids to the closely coupled C–O stretching mode. A reasonably close correspondence of the infra-red and Raman frequencies of the COOH group in this region may be expected for these acids since such a coincidence of the COOH frequencies have been noted in trichloroacetic acid by the above authors. The probable assignments of the frequencies in this region has been indicated in Table I last column, for these two acids. There is a group of five lines

TABLE I

Oxalic acid dihydrate $(COOH)_2 \times 2H_2O$	Malonic acid $(COOH)_2 \cdot CH_2$		Succinic acid $(COOH)_2 \cdot (CH_2)_2$			Assignment
Marignan and Bardet (Raman effect)	Author (Raman effect)	Infra-red	Author:	R. Theimer and O. Theimer (Raman Effect)	Infra-red	
1	2	3	4	5	6	7
270 (2)	..	..	387 (5)	..	..	C–C bending
422 (2)	407 (1)	..	..	..	..	Asymmetrical twisting or bending of the molecular frame work
482 (8)	432 (1)	..	..	..	..	
573–	572 (1)	..	..	..	..	..
	579 (1)	..	..	..	..	
				629 (0)	..	
			683 (1)	681 (0)	..	O=C<O angle deformation modes
				706 (00)		
737 (1)	..	..	..	740 (00)	747±5	
	767 (5)	765± 7				
791 (3)	..	..	..	803 (00)	..	..
	..	..	..	..	834±6	..
850 (2)	..	..	..	..	..	..
857 (20)	897 (1)	894± 4	..	..	..	..
	906 (1)	..	939 (8)	938	925	
	924 (8)	922	..	..	..	
	941 (2)	..	958 (0)	..	..	C–C chain vibrations
	963 (1)	..	965 (0)	..	..	
	976 (1)	987± 4	985 (0)	..	..	
	..	1070±12	1090 (1)	1093	1053	
	1181 (2)	1170	..	..	1150	Oscillations involving C-O-H-group
	1231 (1)	1206± 7	1233 (3)	1230	..	
			1246 (2)			
	..	..	..	..	1275± 8	..
	1289 (1)	..	1292 (2)	1295	..	CH_2 deformation
	1305 (0)	..				
	1317 (0)	1311	1315 (0)	..	1314	Closely coupled O–H deformation ?

TABLE I—*Contd.*

Oxalic acid dihydrate $(COOH)_2 \times 2H_2O$	Malonic acid $(COOH)_2 \cdot CH_2$		Succinic acid $(COOH)_2 \cdot (CH_2)_2$			Assignment
Marignan and Bardet (Raman effect)	Author (Raman effect)	Infra-red	Author; R. Theimer and O. Theimer (Raman Effect)		Infra-red	
1	2	3	4	5	6	7
	..	..	1324 (0) 1344 (0)	..	..	CH_2 deformation
1355 (2) 1365 (3)	..	..	1352 (0) 1365 (3)	..	..	Carboxyl vibrations
..	..	..	1373 (3)	1373	..	Methylene deformation
1487 (3)	1403 (9)	1410	1421 (8)	1421	1417	Oscillation ?
1493 (5)	1429 (3)	1437	1431 (8)			
..	1441 (3)	..	1447 (1)		..	CH_2 deformation ?
			1459 (1)			
..	..	..	..	..	1505	..
1620– 1628–	1645 (8) 1681 (8)	1696	1659 (7)	1650	1641 1700 ± 5	C=O frequency
1739 (8)	..	..	..	..	..	..
1749–	..	1740 ± 5	..	..	..	..
..	..	..	..	..	1788	..
..	..	1943	..	..	..	..
..	..	2500	2590 (0)	2578 (0) 2660 (0)	2500	O–H frequency lowered due to hydrogen bond formation
	2880 (0)	to	2835 (0)	2823 (0)	to	
..	2954 (20)	2950	2931 (15)	2922		Symmetrical C–H stretching
..	2991 (15)	..	2972 (12)	2962	3000	Asymmetrical C–H stretching
3427	..	..	..	..	..	..
3469 (very intense)	..	..	..	..	..	..

in β-succinic acid centered about 1352 cm.$^{-1}$ The spectrum of oxalic acid dihydrate exhibits two lines at 1355 and 1365 cm.$^{-1}$ due to carboxyl group frequencies. Thus the lines at 1324, 1344 and 1373 cm.$^{-1}$ in β-succinic acid may be due to methylene deformation modes and the remaining two lines are obviously carboxyl group vibrations. Hadzi and Sheppard (1953) have concluded by detailed experimental investigations on dimeric acids that the O–H in plane deformation vibrations are connected with frequencies occurring near 1420 and 1300 cm.$^{-1}$ in both infra-red and Raman spectra due to the interaction with the C–O stretching mode. Hence it is not possible to attribute any particular line unequivocally to these modes. It is also seen that a large number of methylene deformation frequencies are observed in β-succinic acid in the region above 1300 cm.$^{-1}$ whereas only a smaller number of lines have been recorded in β-malonic acid. This is what should be expected as there are two methylene groups in succinic acid. The line at 924 cm.$^{-1}$ in β-malonic acid coincides closely with the infra-red absorption maximum at 922 cm.$^{-1}$ reported by Hadzi and Sheppard (1953) which had been attributed by them to the infra-red active out of plane OH deformation mode.

(*b*) *External frequencies.*—Both malonic and succinic acid crystallise in two different crystal forms, namely, α and β forms (Dupre La Tour, 1931). The β form of malonic acid obtained by slow evaporation of a saturated solution in water is triclinic with space group C_i^1. According to Goedkoop and MacGillavry (1957) the unit cell parameters are $a = 5{\cdot}33$ Å, $b = 5{\cdot}14$ Å, $c = 11{\cdot}25$ Å, $\alpha = 102°\ 42'$, $\beta = 135°\ 10'$, $\gamma = 85°\ 10'$. The unit cell of malonic acid contains two molecules. Molecules are arranged in zig-zag chains along the *c*-axis with the carboxyl groups linked through two hydrogen bonds. The β-form of succinic acid grown from a saturated solution in water is stable below 137° C. and belongs to monoclinic prismatic class, space group $P2_1a$ (C_{2h}^5) with two molecules in the unit cell. According to Broadley *et al.* (1959) its parameters are $a = 5{\cdot}126$ Å, $b = 8{\cdot}880$ Å, $c = 7{\cdot}619$ Å and $\beta = 133°\ 36'$. The carboxyl groups are linked through two hydrogen bonds. The observed lattice spectra of these two acids along with that of oxalic acid dihydrate reported by Marignan and Bardet (1952) are given in Table II. Visual estimates of the intensities of the lines are given within brackets.

The recorded spectrum of β-malonic acid exhibits 8 low frequency Raman lines of which the 118 and 125 cm.$^{-1}$ are extremely feeble. A group theoretical analysis of the lattice spectrum of β-malonic acid has been worked out (see Table III). It is seen that of the six lattice oscillations allowed in Raman effect three are of the rotatory type and three are of the translatory type. Of

the eight lattice lines recorded in the spectrum of β-malonic acid only three lines at 52, 90 and 144 cm.$^{-1}$ are intense and these can therefore be assigned to the three rotational modes (Rousset, 1941; 1947). The three less intense lines at 152, 161 and 175 cm.$^{-1}$ may be attributed to the three translatory

TABLE II

Oxalic acid dihydrate	β-malonic acid	β-succinic acid
Marignan and Bardet	Author	Author
51 (13)	52 (20)	..
83 (17)	90 (15)	80 (20)
116 (13)	118 (0)	..
123 (20)	125 (0)	121 (0)
..	..	135 (5)
..	144 (5)	..
151 (2)	152 (2)	..
161 (0)	161 (1)	160 (2)
176 (5)	175 (1)	..

TABLE III

C_i^1	E	i	T	T′	R′	Selection rules	
						Raman	Infra-red
A_g ..	1	1	0	3	3	*p*	*f*
A_u ..	1	−1	3	0	3	*f*	*p*
U_x (S) ..	2	0	..	..	..	..	..
U_x (S−V) ..	2	0	..	..	..	..	..
$h_\rho\chi_\rho$ (T′) ..	3	3	..	..	..	..	..
$h_\rho\chi_\rho'$ (R′) ..	6	0	..	..	..	..	..

p = permitted; *f* = forbidden.

modes. The origin of the extremely feeble lines at 118 and 125 cm.$^{-1}$ is however not quite clear.

The group theoretical analysis of the lattice spectrum of β-succinic acid is given in Table IV.

TABLE IV

C_{2h}^5	E	C_2	i	σ_h	T	T′	R′	Selection rules: Raman	Selection rules: Infra-red
A_1 ..	1	1	1	1	0	0	3	p	f
A_2 ..	1	−1	1	−1	0	0	3	p	f
B_1 ..	1	1	−1	−1	1	2	0	f	p
B_2 ..	1	−1	−1	1	2	1	0	f	p
U_n (S) ..	2	0	2	0	..	..	..	..	..
U_n (S−V) ..	2	0	2	0	..	..	..	..	..
$h_\rho\chi_\rho'$ (T) ..	3	−1	−3	1	..	..	..	..	..
$h_\rho\chi_\rho'$ (T′) ..	3	1	−3	−1	..	..	..	..	..
$h_\rho\chi_\rho'$ (R′) ..	6	0	6	0	..	..	..	..	..

p = permitted; f = forbidden.

It is seen that three each of A_1 and A_2 class of Raman lines of rotatory type alone are permitted to appear in Raman effect. Bhagavantam (1951) has shown that in the case of naphthalene and diphenyl crystals that the three modes coming under A_1 differ from those coming under A_2 only in the matter of the relative phase difference between the two molecules and if the inter-molecular forces are not appreciable the frequencies of the two types of modes may not be appreciably different. The three intense lattice lines at 80, 135 and 160 cm.$^{-1}$ of β-succinic acid can be assigned to the three rotational modes.

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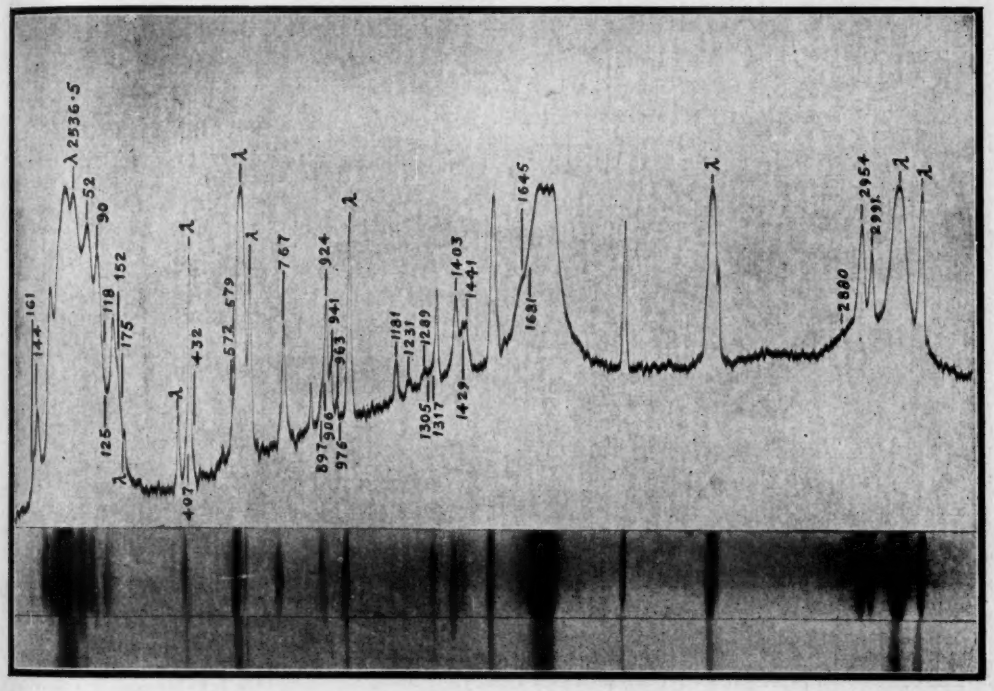

FIG. 1. (Top) Microphotometer Tracing of the Raman Spectrum of β-Malonic Acid.
(Middle) Raman Spectrum.
(Bottom) Mercury Spectrum.

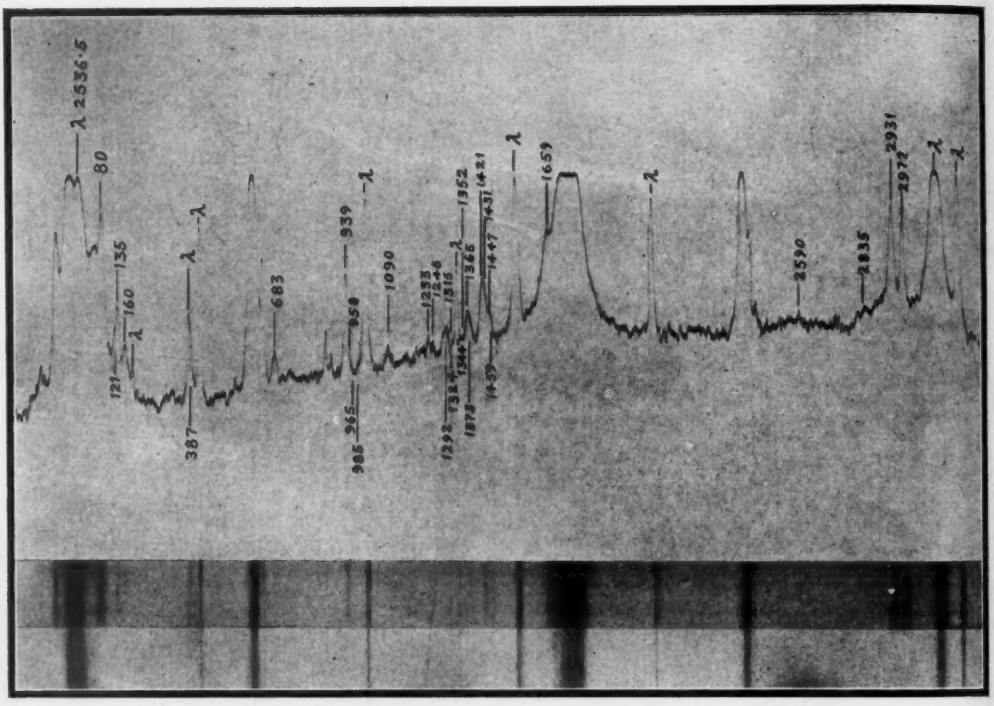

FIG. 2. (Top) Microphotometer Tracing of the Raman Spectrum of β-Succinic Acid.
(Middle) Raman Spectrum.
(Bottom) Mercury Spectrum.

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Summary

Raman spectra of single crystals of β-malonic acid and β-succinic acid have been photographed using λ 2536·5 radiation. 32 Raman lines have been recorded in the case of β-malonic acid. Of these 21 lines have been recorded for the first time. The three intense lattice lines at 52, 90 and 144 cm.$^{-1}$ have been attributed to rotational lattice oscillations. 29 Raman lines in the case of β-succinic acid have been recorded. The entire lattice spectrum and many internal frequencies have been recorded for the first time. The three intense lattice lines at 80, 135 and 160 cm.$^{-1}$ have been assigned to the rotational oscillations of the two molecules of the succinic acid in the unit cell.

References

1. Anand, B. .. *Proc. Ind. Acad. Sci.*, 1936, **4**, 603.
2. Bhagavantam, S. .. *Theory of Groups and its Application to Physical Problems*, 1951, p. 146.
3. Broadley, J. S. *et al.* .. *Proc. Roy. Soc.* (London), 1959, **251 A**, 441.
4. Dupre La Tour, M. F. .. *C.R. Acad. Sci.*, 1931, **193**, 180.
5. Edsall, J. T. .. *J. Chem. Phys.*, 1937, **5**, 509.
6. Fichter, R. .. *Helv. Phys. Acta*, 1940, **13**, 217; 1940, **13**, 309.
7. Flett, M. St. C. .. *J. Chem. Soc.*, 1951, Part II, 962.
8. Goedkoop, J. A. and MacGillavry .. *Acta Cryst.*, 1957, **10**, 125.
9. Hadzi, D. and Sheppard, N. .. *Proc. Roy. Soc.* (London), 1953, **216 A**, 247.
10. Kastler, A. and Rousset, A. *C.R. Acad. Sci.*, 1941, **212**, 645; *Journal de Physique*, 1941, **2**, 49.
11. Lord, R. C. and Merrifield, R. E. *J. Chem. Phys.*, 1953, **21**, 166.
12. Marignan and Bardet .. *C.R. Acad. Sci.*, 1952, **234**, 714, 1964.
13. Peyches .. *Bull. Soc. Chim. France*, 1934, **5** (2), 2195.
14. Rousset, A. .. *La diffusion de la lumiere par les Molecules rigides*, 1947.
15. Theimer, R. and Theimer, O. *MH. Chem.*, 1950, **81**, 313.
16. Wehrli, M. .. *Helv. Phys. Acta*, 1941, **14**, 516.

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